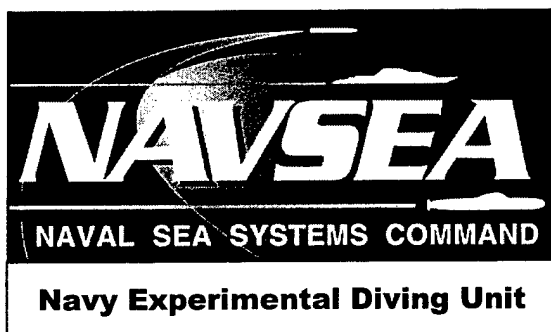


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**DEVELOPMENT OF OXYGEN MONITORING CAPABILITY FOR THE EXISTING
HYPERBARIC CARBON DIOXIDE ANALYZER USED IN DRY DECK SHELTER
OPERATIONS**



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BACKGROUND

The Dry Deck Shelter (DDS) is a hyperbaric system used on submarines to transport SEAL delivery vehicles (SDVs) into an operating area. The system uses air from submarine banks to ventilate the DDS for carbon dioxide (CO₂) removal and provide breathing air to the divers. In order to improve the efficiency of ventilation, the Naval Medical Research Institute (NMRI, now the Naval Medical Research Center (NMRC)) previously developed a portable hyperbaric analyzer (Model HB 1.1, Geotechnical Instruments, Inc., Leamington Spa, U.K.) for monitoring CO₂ within DDSs¹. This analyzer was approved by NAVSEA (PMS-395) in 1998 as the primary control of ventilation during DDS operations². For this purpose, the analyzers are carried into each of the three compartments of the DDS and mounted. Ventilation can then be adjusted in response to changes in measured CO₂ levels within the DDS. This procedure minimizes use of air bank gas during operations while ensuring that ventilation is sufficient to avoid excessive CO₂.

When divers operating from the DDS develop decompression sickness, they can be treated in the chamber compartment of the DDS using recompression and oxygen (O₂) for breathing. The O₂ is delivered to the divers during treatment via masks connected to the built-in-breathing system (BIBS) supplied by an O₂ bank that is part of the DDS system. Concern exists about leakage of O₂ from the masks producing a rise in the O₂ levels within the chamber, thus increasing the fire hazard. Unfortunately, the existing O₂ analyzers, currently used inside the DDS chamber during treatments, are considered unreliable. Consequently, the Naval Sea Systems Command (NAVSEA (PMS-395)) tasked NMRC in August 1998 to add an O₂ monitoring capability to the hyperbaric CO₂ analyzers now used inside the DDS³. This report describes this effort.

TASK OUTLINE

The task is outlined below:

1. Define the requirements for O₂ monitoring in the DDS and gain NAVSEA approval prior to proceeding.
2. Work with Geotechnical Instruments, Inc. (the manufacturer of the DDS hyperbaric CO₂ analyzer) to select commercially available O₂ sensors for incorporation into the CO₂ analyzer.
3. Test prototype CO₂/O₂ analyzers (fitted with candidate O₂ sensors) in laboratory and modify where necessary.
4. Test the final version of analyzer in laboratory.
5. Deliver a recommendation to NAVSEA regarding the use of the analyzer for DDS operations.

ANALYZER DEVELOPMENT

ANALYZER REQUIREMENTS

Requirements used to develop the current hyperbaric analyzer for monitoring CO₂ inside the DDS were given in a previous report¹. The requirements listed below for the current task include: 1) previous requirements (CO₂ analyzer) that are relevant to O₂ monitoring (noted by an *), and 2) additional requirements specific to O₂ measurement.

Essential Requirements.

1. Oxygen measurement range and units: 0 to 2 atmospheres absolute (ATA) O₂.

This measurement range extends beyond the maximum partial pressure oxygen (PO₂) that would be expected to occur within the DDS chamber atmosphere in the event of O₂ leakage during treatments.

2. Operating pressure range: 1 to 6 ATA.*

This meets the pressure range of DDS compartments during operations.

3. Hyperbaric chamber safe.*

The analyzer must be able to be operated safely (i.e., not inducing fires or explosions) inside a hyperbaric chamber exposed to high-pressure O₂ mixtures. Offgassing of volatile contaminants must be below acceptable U.S. Navy limits for diving systems.

4. Ambient temperature range: 10 to 35 °C.*

This requirement is expected to bracket the DDS operational temperature range.

5. Water resistant.*

Analyzers will be exposed to high humidity and probably have some water contact (including accidental dropping into the water) during DDS floodups. Some protection against failure under these conditions should exist.

6. Relative humidity: Dry to ~90 to 100%.*

The high humidity requirement reflects the conditions inside the DDS as given in item five.

7. Powered by rechargeable battery, continuous analyzer operation without recharging >8 h.*

Analyzer batteries are expected to be checked and recharged, if necessary, immediately prior to DDS operations. Analyzers will be removed from the charger and installed in DDS compartments where they will be operated on battery power. Required eight-hour analyzer operation without recharging should ensure sufficient battery life during all DDS operations.

Desired, but not Essential Requirements.

1. Short-term O₂ measurement repeatability (within 10 minutes): $\pm 5\%$ relative over measurement and pressure range, as determined in the laboratory.

A well-designed analyzer should easily meet this level of precision.

2. Short-term O₂ accuracy (within 24 h of calibration): $\pm 5\%$ relative over measurement and pressure range, as determined in the laboratory.

There is no official requirement for O₂ measurement accuracy in the DDS. However, $\pm 5\%$ accuracy observed for O₂ in the laboratory should meet the need for reliable monitoring of O₂ levels even assuming a doubling of the error in the field.

3. Calibration: One point span at ~ 0.209 ATA O₂ (20.9% O₂ span gas at 1 ATA).

Calibration at 1 ATA using 20.9% O₂ (air) as the standard is probably the most practical approach in the field and should maximize accuracy at this pressure/concentration point. This latter reason is particularly important as air is used for recompression treatment in the DDS. There are also likely to be more alternative sources of calibration air (or equivalent) available in the field if needed. One alternative would be the gas standard used for calibrating the Central Atmosphere Monitoring System (CAMS-I) on U.S. submarines, which contains $\sim 20.9\%$ O₂ in nitrogen (N₂) with a few other components. However, because most O₂ sensors require zeroing, the desired one-point span calibration (without zeroing) may not be possible.

4. Response time: Less than 60 seconds to 95% of reading.

This should be more than adequate, as O₂ concentrations within the DDS should not change very quickly.

SELECTION OF O₂ SENSOR

The analyzer manufacturer (Geotechnical Instruments, Inc.) recommended the initial candidate O₂ sensor sold by Seatronics (Model HB, Sunset Commons, PA). Extensive testing revealed serious measurement inaccuracies due to large effects of ambient pressure on O₂ readout. Consequently, after considerable discussion and review of alternative sensors, the Teledyne line of micro-fuel cells (Teledyne Analytical Instruments, City of Industry, CA) was chosen as the second candidate for testing. Preliminary testing of the Teledyne B1 sensor indicated good performance but limited

expected lifetime (eight months in air, according to Teledyne) due to its relatively thin sensor membrane. In fact, during testing, one B1 sensor failed due to membrane rupture during pressure exposure. As a result, B3 and C3 sensors, with their thicker sensor membranes and longer expected lives (12 and 18 months, respectively), were each installed in two test analyzers and evaluated. Results showed that all three types of Teledyne sensors performed similarly as configured in the hyperbaric analyzer (Fig. 1). Consequently, the C3, with the longest expected life, was chosen for final testing in the hyperbaric analyzer.

MODIFICATIONS OF CANDIDATE ANALYZER

Final changes to the original hyperbaric CO₂ analyzer consisted of internal installation of the O₂ sensor and software modifications allowing O₂ calibration and display along with CO₂ and depth. Thus, the outward appearance of the CO₂/O₂ analyzer is indistinguishable from the original CO₂ analyzer with the exception of the O₂ partial pressure added to the display. These changes allow the measurement of O₂ at partial pressures up to 2 atmospheres absolute (ATA) at ambient pressures from 1 to 6 ATA. This is in addition to the existing ability to measure CO₂ up to 25,000 ppm (2.5%) surface equivalent value (SEV).

DESCRIPTION OF FINAL ANALYZER

The final analyzer with both CO₂ and O₂ measurement capability was designated a new product line by the manufacturer: Anagas Hyperbaric Analyzer; Model HB 1.2. This model number contrasts with the CO₂-only Model HB 1.1 although both models are very similar. Consequently, much of the description here is the same for both units but is repeated for completeness. The Geotechnical product number for the U.S. Navy version of their HB 1.2 is 1.2A. The HB 1.2A unit includes the analyzer with measurement range of 0-25,000 ppm (2.5%) CO₂ SEV and 0-2 ATA PO₂, blue analyzer case, battery charger, blue carry case, battery case sealed with silicone rubber and an aluminized adhesive label, five spare Teflon filters, and an operating manual.

This analyzer, like Model HB 1.1, can be operated up to 6 ATA and uses non-dispersive infrared detection for measuring CO₂. For O₂, a Teledyne micro-fuel cell (C3) is used. The expected 18-month lifetime of the O₂ sensor suggests that sensor replacement may normally only be necessary when analyzers are returned to the manufacturer for yearly service. However, only experience in the field will confirm whether this is true. A low-voltage backlight allows the digital display to be easily read in the DDS. The sample pump, with brushless motor, draws ~ 500 ml/min (at 1 ATA) of sample gas into the analyzer.

Readout for CO₂ is presented in ppm units to the nearest 20 ppm in the display window. Readout for O₂ is given in ppATA to the nearest 0.001 ppATA in the upper right corner of the display. PO₂ readout can be toggled with a single keystroke to display gauge pressure in units of feet of seawater (fsw). Analyzers are calibrated for CO₂ by presenting a span gas; no zero gas is used. The concentration of the calibration gas is

entered to the nearest 1 ppm. Calibration for O₂ is done by first zeroing with a zero gas and then presenting a span gas and entering the concentration to the nearest 0.001 ppATA. Following a step change in CO₂ and O₂ concentration, analyzer reading stabilizes after approximately 40 seconds.

The analyzer can be operated in wet, humid conditions at temperatures ranging from 0 to 40 °C. If dropped into water, the instrument will float. If water enters the gas inlet, it will be trapped in the inlet filter and the sampling pump will automatically shut off. The analyzer can be restarted by removing the filter and replacing it or blowing it out by mouth or gentle gas flow. For DDS use, the analyzer is run off its self-contained NiCad batteries. Overnight charging provides approximately 12 h of usage. For applications other than DDS, the analyzer can be used when it is attached to the charger that plugs into 110-volt line current. However, the instrument must have batteries in place to operate.

ANALYZER TESTING

This report describes the laboratory testing and results from four analyzers containing the final modifications including the Teledyne C3 O₂ sensor.

SUMMARY

Following retrofitting of four analyzers with the Teledyne C3 O₂ sensor, a four-week period of testing was conducted in the laboratory during August 1999. For discussion purposes, these analyzers will simply be referred to as #1-4. Although the major purpose of this testing was to evaluate short-term performance of O₂ measurement at the surface and under pressure, CO₂ performance in these modified units was also examined. This was done to confirm that the O₂ modifications had no adverse effects on CO₂ measurement. Testing involved procedures similar to those used previously during development of the original analyzer¹. Consequently, some of the description of procedures below is taken from this earlier study. Briefly, analyzers were tested for 1) precision at surface, and 2) accuracy at surface and at pressure, both immediately and 24 h after calibration. No long-term testing was done to determine potential problems with O₂ sensor life after repeated hyperbaric exposure. Also, no testing was done to show how the O₂ sensor performs in the field and actually tolerates DDS conditions.

HYPERBARIC TEST SYSTEM

The specially designed hyperbaric test system, used previously and described in detail in Reference (1), allowed controlled delivery of test gases to multiple analyzers under pressure (**Fig. 2**). This system included a hyperbaric chamber configured with a gas manifold system that could handle up to seven different test gas standards, as well as a cylinder of CO₂-free air (i.e., zero air).

Inside the chamber, up to four analyzers were connected to the gas delivery circuit to sample gas from a flowing stream that was designed (as described in Reference (1)) to maintain a small excess flow of ~500 ml/min over what the analyzers consumed via their sample pump. This ensured that the analyzers sampled only test gas, and not ambient air, and that minimal back pressure (<1 psi) was placed on the flow to the analyzer.

The chamber, rated well beyond the maximum test pressure of 6 ATA, was equipped with separate air supply and decompression circuits so that it could be compressed with air or decompressed at precise rates. The travel rate for testing in this study was 1 fsw/s during compression and ~2 fsw/s during decompression. For analyzer testing, chamber pressure was monitored from a Heise pressure gauge (Dresser Industries Instrument Division, Newtown, CT) readable to the nearest 0.5 fsw. This gauge had been calibrated several years prior to testing with a pressure comparator certified with pressure standards traceable to the National Institute of Standards and Technology (NIST) which should produce accuracy of $\pm 0.1\%$ full scale (450 fsw) at time of calibration. The change in accuracy over the several years following calibration is unknown. The temperature of the chamber was controlled to within 0.5 °C of the set point of 21 °C (Yellow Springs Instrument Co., Yellow Springs, OH).

LABORATORY TESTING

Instruments were stored, calibrated, and tested (other than inside the hyperbaric chamber) at laboratory temperatures ranging between 19 and 24 °C. Occasionally, overnight storage temperatures were several degrees Centigrade outside of this range due to problems with the control of building temperature. Analyzers were recharged the night before each day's testing by connecting the battery charger, which was plugged into line power. The charger was disconnected the next day prior to calibration and testing so that all procedures were done with analyzers running on battery power. All four analyzers were tested weekly during the four-week evaluation period.

The following gases were used during testing:

1. Zero N₂: CO₂-free, hydrocarbon-free.
2. Eight gravimetric standards of 1,500 to 25,000 ppm CO₂, balance hydrocarbon-free air (20.9% O₂).

All standards were obtained commercially, and certified to $\pm 1\%$ relative.

Analyzers were tested in two locations in the laboratory: 1) on the laboratory counter at ambient pressure, and 2) inside the hyperbaric chamber at pressures up to 6 ATA. In both cases, gas was delivered to one or more analyzers simultaneously via a branching circuit (**Figs. 2-3**) made of wide-bore (3/16 inch inner diameter) Tygon tubing and plastic tees so that a slight excess of gas exited the overflow. As discussed before, this ensured that only test gas, not ambient air, was sampled. For countertop testing,

overflow was adjusted to several liters/minute; adjustment of flow inside the hyperbaric chamber was described above. No effect on instrument reading was observed when gas flow to the instruments was varied over a wide range both on the counter and in the chamber up to 6 ATA.

On the counter, gas was supplied to the analyzers via the branching circuit using a precision gas divider (STEC Model SGD-701, Horiba Instruments, Inc., Ann Arbor, MI; **Fig. 3**). The STEC device allowed blending of the gas standards with a diluent gas (zero N₂) in 10 equal steps from 0 to 100% of the standard CO₂ and O₂ concentrations. Teflon tubing was used to connect the standards and diluent gases to the STEC. This gas divider was previously shown to be linear to within the manufacturer specification of $\pm 0.5\%$ of full scale, as described in Reference (1). With the STEC, an entire response curve could be generated from the 10 concentrations produced from a single gas standard.

Analyzers were turned on at the beginning of each test day, disconnected from the battery charger, and batteries verified as fully charged. Analyzers were then allowed to warm up for at least five minutes. Analyzers were calibrated together on the counter at ambient pressure, unless the protocol indicated otherwise. All calibration readings were taken after analyzers had stabilized, which typically took approximately 40 seconds following a gas switch. Calibration for CO₂ was done by spanning the instrument with a nominal 15,000 ppm (1.5%) standard. This required calculating the ppm CO₂ SEV of the gas delivered from the gas standard to the analyzers:

$$\text{SEV concentration (ppm CO}_2\text{)} = \text{gas standard concentration (ppm CO}_2\text{)}^* \\ (\text{STEC setting}/100) * \text{barometric pressure (bars)}/1,000 * 0.98692$$

where the gas is delivered via the STEC device or

$$\text{SEV concentration (ppm CO}_2\text{)} = \text{gas standard concentration} * \\ \text{barometric pressure (bars)}/1,000 * 0.98692$$

where the gas is delivered directly.

This calculation was necessary as the analyzers compensate for absolute pressure and display CO₂ concentrations in SEV. Laboratory barometric pressure was measured in bars using a digital barometer with a specified accuracy of 0.1% (Model AG-200B; Sensotec, Inc., Columbus, OH), calibrated using equipment traceable to NIST. The factor, 0.98692, is used to convert bars to atmospheres. The SEV CO₂ concentration calculated in this manner was used not only for calibration but also to define expected analyzer readings during testing using the different gas standards. Zero N₂ was then delivered to the analyzers and the reading recorded; no zero adjustment for CO₂ was possible. Calibration for O₂ was then done by first zeroing with zero N₂ and then

spanning with air (20.9% = 0.209 ATA O₂ at 1 ATA). No correction for barometric pressure was done for O₂ calibration.

Analyzer readings during actual testing were taken using the "ID" function for data storage. For testing on the laboratory counter, each data point was manually stored into instrument memory, after readings had stabilized, using the #6 "store" key. During testing inside the hyperbaric chamber, analyzers were put in the logging mode, which allowed automatic recording of data at set intervals. For this application, the logging interval was set to one minute, and pump duration set at 59 seconds, which made the sample pump run continuously and recorded one reading into instrument memory every minute. At the end of each test, data in memory was downloaded to a personal computer using UNICOM Analyzer Download Software, version 1.06 (Geotechnical Instruments, Inc.), and manipulated using spreadsheet software.

Analyzers were tested for the following:

1. Ambient Pressure Precision/Accuracy.

a. Procedures. On the first day of this test, calibrated instruments were presented with 15,000 ppm (1.5%) CO₂, 12% O₂, balance N₂. These concentrations were delivered using the STEC set at 60% with the 25,000 ppm CO₂ standard (balance air) and zero N₂ for the diluent. This was repeatedly done five times over a 30-60 minute period and measurements recorded. Calibration was then checked and each analyzer recalibrated if not within 400 ppm CO₂ or 0.005 ATA O₂. STEC response curves were then generated by varying the STEC setting from 0 to 100% and back to 0, using first the 25,000 ppm (2.5%) CO₂, then a 2,500 ppm (0.25%), standard. Analyzers were then turned off. Total test time was one to two hours. The second day, calibration of each analyzer was checked, but not readjusted, and zero N₂ measured prior to repeating the STEC curves as done the first day.

b. Rationale. These tests defined precision and linearity of instruments at ambient pressure over approximately a 24-hour period, which should be longer than analyzers are used in the field without recalibration.

2. Hyperbaric Accuracy.

a. Procedures. On the first day of this test, calibrated instruments were put into the hyperbaric chamber, which was set at 21 °C (± 0.5 °C). Five minutes were allowed for equilibration. Gas standards were then delivered to the analyzers at pressures up to 6 ATA, according to **Table 1**, which restricted testing up to 25,000 ppm (2.5%) CO₂ SEV. Testing began with the lowest CO₂ standard at 1 ATA. Pressure was then increased in 1 ATA steps up to the maximum pressure for each gas standard and then back to 1 ATA, waiting at each new pressure for three minutes for readings to stabilize before recording. Testing was repeated with the other standards in order of increasing CO₂ concentration

and up to the maximum test pressures in **Table 1**. Analyzers were then turned off. Total test time was three hours.

The second day, calibration (including delivery of zero N₂) of each analyzer was checked, but not readjusted, prior to repeating the hyperbaric testing as during the first day. When this testing was completed, the analyzers were reset to factory calibration (for both CO₂ and O₂) by performing several keypad strokes, and hyperbaric testing was again repeated. Analyzers were then turned off. Total test time was six hours.

b. Rationale. These tests defined instrument performance over approximately a 24-hour period at CO₂ and O₂ concentrations across absolute pressures that span the range of operating exposures. Resetting to factory calibration was evaluated as an option in the field if normal calibration cannot be done.

3. Offgas Testing.

a. Procedures. One analyzer was tested for offgassing by using a 10 l Tedlar bag (SKC Inc., Eighty Four, PA) that has low permeability and is designed for accurate sampling of trace levels of contaminants in air. The Tedlar bag was first filled and emptied three times with hydrocarbon-free gas and filled a fourth time and the bag valve closed. The bag was then stored in the laboratory (19-24 °C) for one day to equilibrate prior to baseline (empty bag) sampling. The bag was sampled by attaching an evacuated 500 ml stainless steel canister to the bag valve and allowing the canister to draw gas out via the bag valve and equilibrate at 1 ATA. The canister was subsequently backfilled to 1 ATA with hydrocarbon-free gas to facilitate sample loading into a gas chromatograph (GC) to screen for contaminants. After baseline testing, the bag was cut open, the analyzer placed into the bag, and the bag secured by twisting the Tedlar to close the opening and attaching a rubber band on the outside. Resampling and analysis of contaminants given off by the analyzer were done after another four days. Gas samples were screened for volatile organic compounds (VOCs) using GC with flame ionization (FID) as described in Reference (1).

b. Rationale. These tests determined if significant levels of volatile contaminants were being released that might be a hazard during use in the Fleet. Test procedures enhanced the ability to detect contaminants by using low permeability test bags and a small gas volume around the analyzer. For these reasons, contaminant levels measured during this test should be much higher than those that might occur during actual analyzer use where there is a large gas space around the analyzer and ventilation of the DDS is being performed.

4. Testing of Displayed Pressure Reading.

No testing of the pressure reading (in fsw) shown on the analyzer display was done.

DATA ANALYSIS

1. Precision.

Means and relative standard deviations were calculated from the precision data.

2. Accuracy.

Accuracy data were used to calculate relative percent error:

$$\text{Relative percent error} = \frac{(\text{Observed reading} - \text{Expected reading})}{\text{Expected reading}} \cdot 100$$

Expected readings were determined as defined earlier.

3. Error in Calibration Gas Standards.

Measurement results will reflect the error of $\pm 1\%$ relative associated with the certified concentrations of the gas standards.

RESULTS AND DISCUSSION

PRECISION

Relative standard deviations based on five measurements of 0.12 ATA O₂ and 15,000 ppm CO₂ over 10 minutes were well below 1% for the four analyzers (**Tables 2-3**). No problem with zero drift was observed with any of the instruments; when presented with zero N₂, the analyzers in all cases read within 0.001 ATA O₂ and 300 ppm CO₂ of zero.

Conclusion. All four analyzers met the desired $\pm 5\%$ short-term repeatability requirement for O₂ and, as previously shown in Reference (1), met this same requirement for CO₂.

AMBIENT PRESSURE ACCURACY

After calibration with 0.209 ATA O₂, the O₂ measurement error at ambient pressure (1 ATA) for all four analyzers was $\leq 5\%$ for PO₂s from 0.21 ATA down to ~ 0.10 ATA (**Fig. 4**, upper graphs). At lower PO₂s, relative errors increased, reflecting the translation of small absolute errors at these levels into large relative errors. Although results suggest that there are differences among analyzers in measurement of O₂, these differences were not large for the four units tested. For a given analyzer, little difference ($< 5\%$) was observed between O₂ results done on two consecutive days without recalibration (**Fig. 4**, lower graphs). No problem with zero drift was observed with any of the instruments; as with the precision testing, when presented with zero N₂, analyzers in all cases read within 0.001 ATA O₂ of zero.

After calibration with 15,000 ppm CO₂, the CO₂ measurement error at ambient pressure for all four analyzers was $\leq 10\%$ for CO₂ concentrations from 25,000 ppm (2.5%) down to ~2,500 ppm (**Fig. 5**, upper graphs). Below ~2,500 ppm, the analyzers had difficulty reading CO₂ levels to within 10%. The accuracy of CO₂ measurement at the low end was somewhat poorer than seen previously with the testing of 19 analyzers during the development phase where analyzers were generally able to measure CO₂ to within 10% down to ~1,500 ppm¹. There, recalibration using 1,000 ppm CO₂ was shown to improve accuracy around this level of CO₂ to $\leq 10\%$. The difference between CO₂ results done on two consecutive days without recalibration (**Fig. 5**, lower bottom) was generally larger than that for O₂ although still $< 5\%$. No problem with zero drift was observed with any of the instruments; again, as with the precision testing, when presented with zero N₂, analyzers in all cases read within 300 ppm CO₂ of zero.

Conclusion. All four analyzers met the desired short-term accuracy requirement at ambient pressures of 1) $\pm 5\%$ for O₂ from 0.21 ATA down to ~0.10 ATA, and 2) $\pm 10\%$ for CO₂ from 25,000 ppm down to ~2,500 ppm.

HYPERBARIC ACCURACY

Relative errors were within 5% for PO₂s from 0.21 to 0.8 ATA when monitoring air at pressures from 1 to 4 ATA (**Fig. 6**, upper graphs). At pressures above 4 ATA, error for PO₂s from ~0.8 to 1.3 ATA increased up to 10% for one analyzer and ~15% for a second analyzer. Compared to ambient pressure testing, there were greater differences among analyzers in their responses to O₂. As was the case with ambient pressure testing, little difference ($< 5\%$) was observed between O₂ results done on two consecutive days without recalibration (**Fig. 6**, lower graphs). After analyzers were reset to factory calibration, relative O₂ measurement error increased substantially in two of the analyzers up to $\pm 15\%$ (**Fig. 7**, upper graphs), and significant shift occurred in the response curves (**Fig. 7**, lower graphs). This suggested that factory settings may be in error in two of the units.

Accuracy of CO₂ measurements was similar to the $\pm 10\%$ relative found previously for CO₂ concentrations from 1,500 to 25,000 ppm (2.5%) SEV at pressures from 1 to 6 ATA (**Fig. 8**, top graphs)¹. This would be expected as the O₂ sensor modification should not affect CO₂ function. Again, significant differences in CO₂ responses were observed among some of the instruments, but little difference ($< 5\%$) seen between results from two consecutive days without recalibration (**Fig. 8**, lower graphs). After analyzers were reset to factory calibration, relative CO₂ measurement error generally remained within 10% (**Fig. 9**, upper graphs), although readings were often substantially different from those obtained with laboratory calibration (**Fig. 9**, lower graphs). The one exception was with analyzer #4, which clearly had a problem with the CO₂ factory settings, something not observed with other analyzers during previous testing¹.

Conclusion. All four analyzers met the desired short-term PO₂ accuracy requirement of $\pm 5\%$ when monitoring air at pressures from 1 to 4 ATA; above 4 ATA, the relative error of two of the analyzers increased up to 10% or 15%. All four analyzers met the desired

short-term CO₂ accuracy requirement of $\pm 10\%$ for CO₂ concentrations from 1,500 to 25,000 ppm (2.5%) SEV at pressures from 1 to 6 ATA. Problems with the factory calibration in some of the analyzers suggest that this procedure may not be a reliable option in the field when normal calibration cannot be done.

GENERAL PERFORMANCE

During the 18-month development period, the four hyperbaric analyzers were tested for several hundred hours in the laboratory. The bulk of this testing was done during the initial process to select an O₂ sensor for the final four-week evaluation. This required frequent shipping of analyzers back and forth between NMRC and Geotechnical Instruments, located in the U.K., for sensor removal and replacement with different candidates. During this time, the major problem encountered was occasional lockup of some of the analyzers when initially compressed. This problem has been reported previously and appears to be linked to flexing of the circuit boards due to inadequate venting of the analyzer case¹. Our experience indicates that after the analyzer case has been opened (for any repair or component replacement), there is a potential for this type of failure to occur. The remedy in the past has generally been the replacement by the factory of one or more of the circuit boards. However, once the analyzer has been shown to tolerate several rapid (~ 2 fsw/s) pressure cycles without incident, the likelihood for failure is low. Unfortunately, this problem still persists despite repeated discussions with Geotechnical Instruments in which we have recommended that all fully assembled analyzers, prior to leaving the factory, be tested for this defect.

During the final four-week testing with the C3 O₂ sensors, no failures occurred and analyzers operated without incident.

OFFGAS TESTING

Only very low levels (<1 ppm total VOCs) of several unknown VOCs were detected during the offgas testing of one analyzer. Because of the low contaminant levels and the fact that these levels would be much lower during actual operational use, no attempt was made to identify the unknown species using mass spectrometry. Although only one analyzer was tested, previous testing of the Geotechnical CO₂ analyzers suggests there is no reason to expect substantial differences in offgassing among analyzers¹.

Conclusion. The low level of offgassing observed from the analyzer tested should cause no safety concern.

SUMMARY

1. There is no official requirement for O₂ measurement accuracy in the DDS. However, the accuracy observed for O₂ in the laboratory should meet the need for reliable monitoring of O₂ levels even assuming a doubling of the error in the field.

2. Accuracy of CO₂ measurement of the four hyperbaric CO₂/O₂ analyzers easily met the 20% accuracy requirement for DDS use recommended by a U.S. Navy Working Group in Reference (4). This finding agrees with that previously reported following initial development of these analyzers two years ago¹.
3. Because neither long-term testing nor evaluation of the CO₂/O₂ analyzers in the field has been performed, analyzer reliability will need to be followed carefully during transition to Fleet use. At this time, the analyzer is only recommended for use in situations where daily access to calibration gas can be assured. The expected 18-month lifetime of the O₂ sensor suggests that sensor replacement may normally only be necessary when analyzers are returned to the manufacturer for the yearly preventive maintenance service. However, only experience in the field will confirm whether this is true.
4. The significant differences among analyzers that were seen during testing suggest that all analyzers be tested in the laboratory for reliability prior to delivery to the Fleet.
5. Analyzers should be operated using procedures given in Appendix A.
6. In addition to meeting the requirements for O₂ and CO₂ measurement during DDS operations, this analyzer may also fill the existing need for reliable O₂ and CO₂ measurement inside other types of hyperbaric chambers and diving apparatus.

REFERENCES

1. R. S. Lillo, W. R. Porter, A. Ruby, W. H. Mints, J. M. Caldwell and J. F. Himm, *Development and Evaluation of Hyperbaric Carbon Dioxide Analyzer for Dry Deck Shelter Operations*, NMRI 98-01, Naval Medical Research Institute, Bethesda, MD, 1998.
2. NAVSEA letter, *Approval of New Technical Manual for Dry Deck Shelter System*, 9086/640CL, Ser 395A23/049 of 5 Mar 98
3. NAVSEA letter, *FY99 Funding Estimates*, 7110/FY99, Ser 395A22/148 of 14 Aug 98
4. Unpublished Minutes of Meeting of the U.S. Navy's Closed Living Space Environmental Concerns Working Group of 14 December 1993, held at the Naval Medical Research Institute, Bethesda, MD.

FIGURE LEGENDS

Figure 1.

Teledyne Sensor Accuracy. Representative measurement error vs. PO_2 and test pressure for a single test with each of three different Teledyne sensors: B1, B3, and C3. Analyzers were calibrated with 0.209 ATA (20.9% O_2 at 1 ATA) and then exposed to the 20.9% O_2 standard as pressure was increased in 1 ATA steps up to 6 ATA and then back to 1 ATA.

Figure 2.

Hyperbaric Test System. Delivers test gases to multiple analyzers under pressure.

Figure 3.

Ambient Pressure Test System. Delivers test gases to multiple analyzers at ambient pressure via the STEC gas divider.

Figure 4.

O_2 Ambient Pressure Accuracy. Measurement error vs. PO_2 for two consecutive test days for each of four weeks. Separate plots are presented on each graph for each of the four different analyzers. Top graph gives the first day results and the bottom graph the difference between day one and day two of each week. Analyzers calibrated with 0.209 ATA (20.9% O_2 at 1 ATA) at the beginning of each week's testing. STEC gas divider then used to deliver 0 to 100 to 0% (in 10% steps) of the 20.9% O_2 standard concentration.

Figure 5.

CO_2 Ambient Pressure Accuracy. Measurement error vs. CO_2 concentration for two consecutive test days for the third week (representative) of a four-week test period. Separate plots are presented on each graph for each of the four different analyzers. Top graph gives the first day results and the bottom graph the difference between day one and day two of the week's testing. Analyzers calibrated with 15,000 ppm CO_2 at the beginning of each week's testing. STEC gas divider then used to deliver 0 to 100 to 0% of the gas standard concentration. Two gas standards used: 2.5% and 0.25% CO_2 , with each standard plotted on separate pairs of graphs as noted at the top of each graph.

Figure 6.

O₂ Hyperbaric Accuracy. Measurement error vs. PO₂ and test pressure for two consecutive test days for each of four weeks. Separate plots are presented on each graph for each of the four different analyzers. Top graph gives the first day results and the bottom graph the difference between day one and day two of each week. Analyzers calibrated with 0.209 ATA (20.9% O₂ at 1 ATA) at the beginning of each week's testing. The 20.9% O₂ standard was then delivered to the analyzers as pressures were varied from 1 to 6 ATA and then back to 1 ATA.

Figure 7.

O₂ Hyperbaric Accuracy – Factory Calibration. Measurement error after analyzers were reset to factory calibration for each of four weeks. Separate plots are presented on each graph for each of the four different analyzers. Top graph gives the factory calibration results and the bottom graph the difference between laboratory calibration (Day 1) and factory calibration.

Figure 8.

CO₂ Hyperbaric Accuracy. Measurement error vs. test pressure for two consecutive test days for the third week (representative) of a four-week test period. Separate pairs of graphs are presented for each of the four different analyzers. Top graph gives the first day results and the bottom graph the difference between day one and day two of each week. Analyzers calibrated with 15,000 ppm CO₂ at the beginning of each week's testing. Seven gas standards (in legend) were then delivered to the analyzers as pressures were varied from 1 to 6 ATA and then back to 1 ATA.

Figure 9.

CO₂ Hyperbaric Accuracy – Factory Calibration. Measurement error after analyzers were reset to factory calibration for the third week (representative) of a four-week test period. Separate pairs of graphs are presented for each of the four different analyzers. Top graph gives the factory calibration results and the bottom graph the difference between laboratory calibration (Day 1) and factory calibration.

Figure 1. Teledyne sensor accuracy.

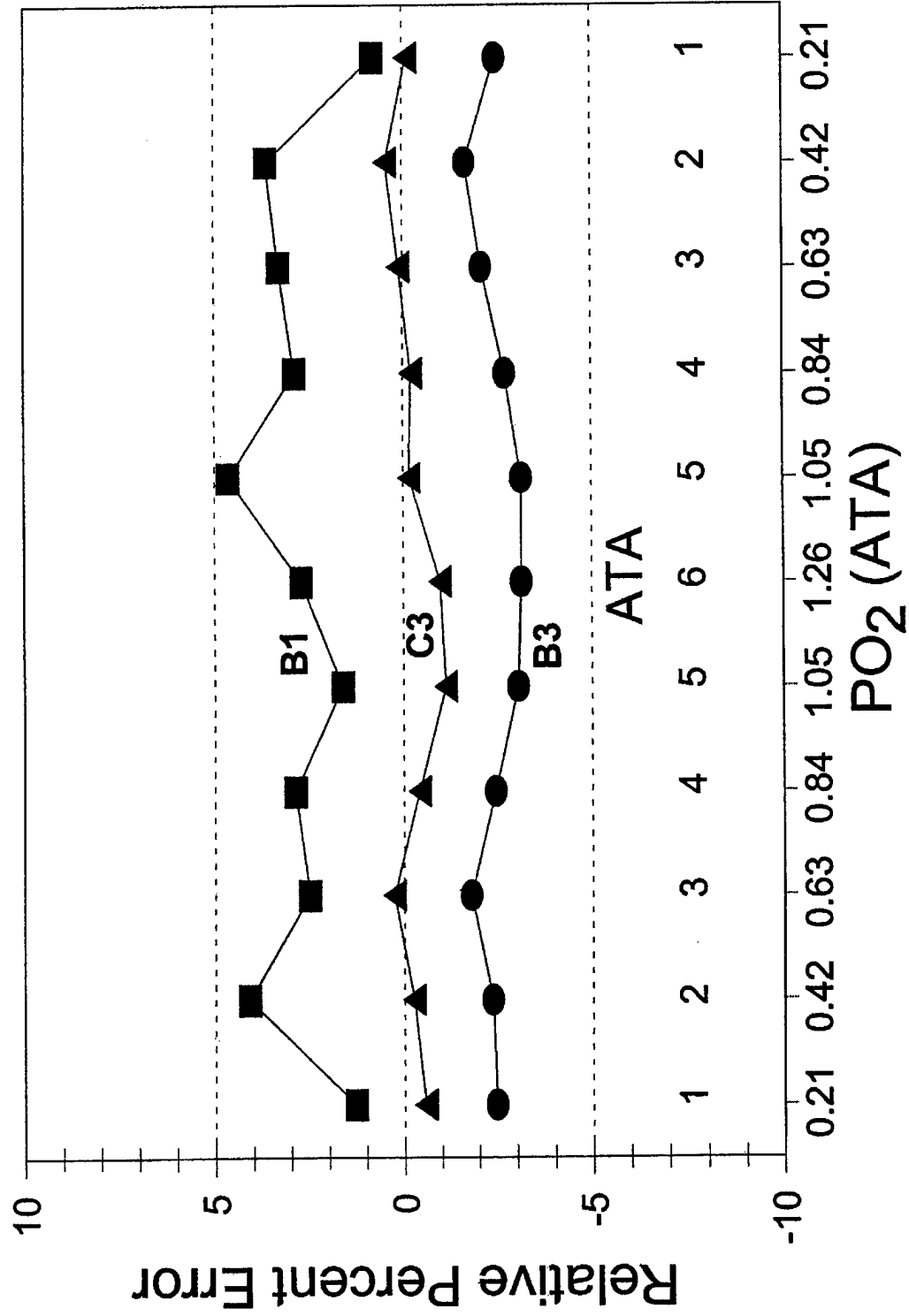


Figure 2. Hyperbaric test system.

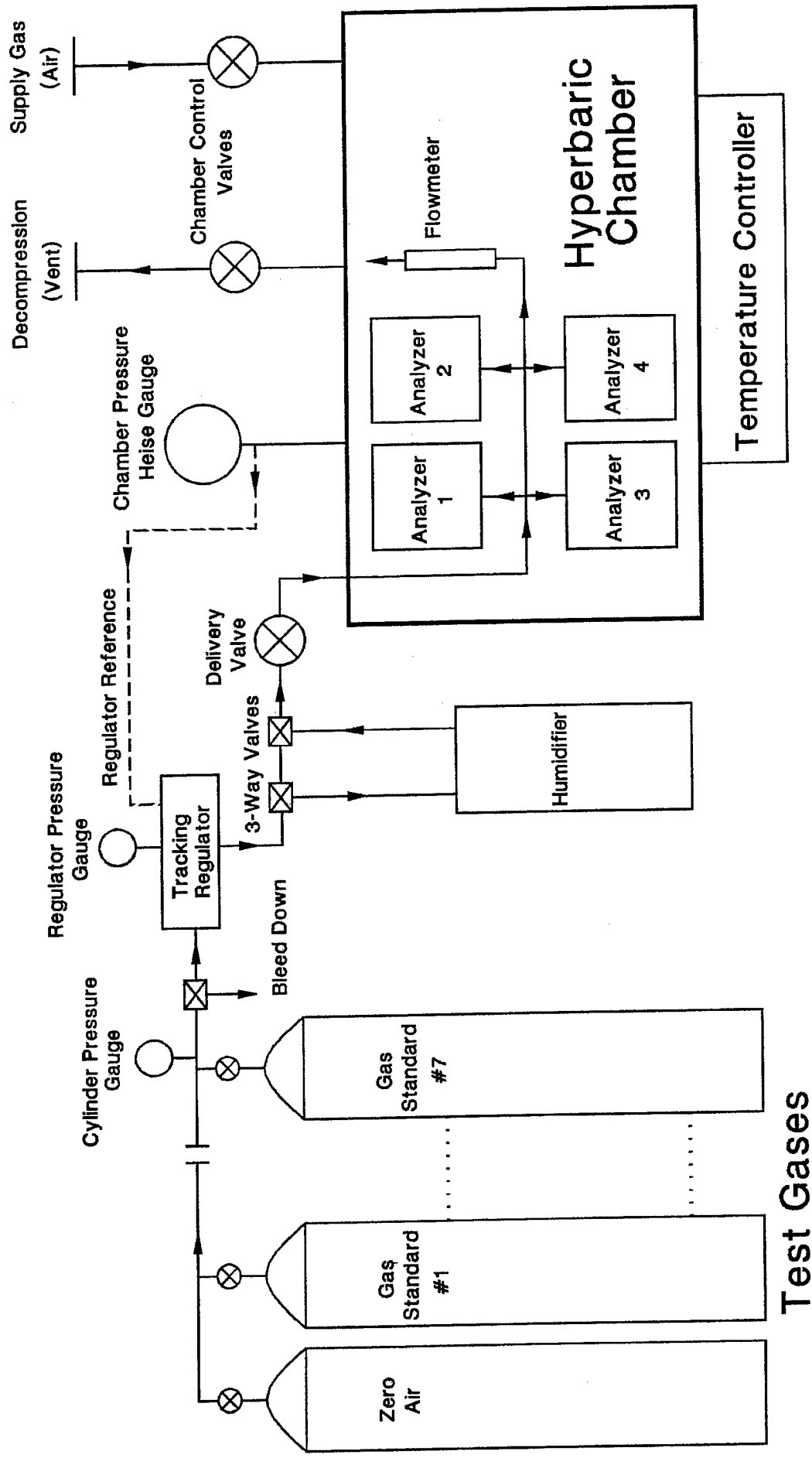


Figure 3. Ambient pressure test system.

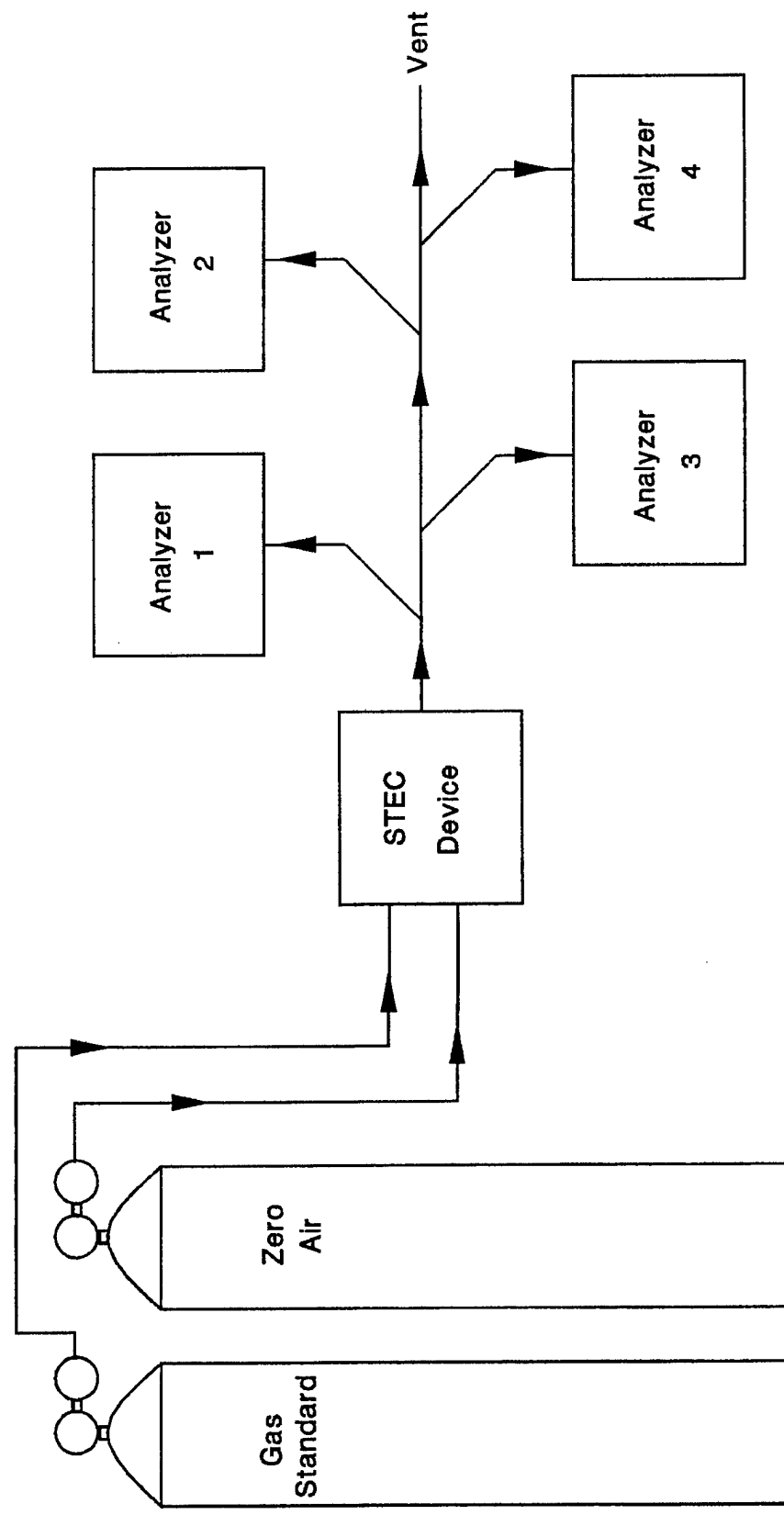


Figure 4. O₂ ambient pressure accuracy.

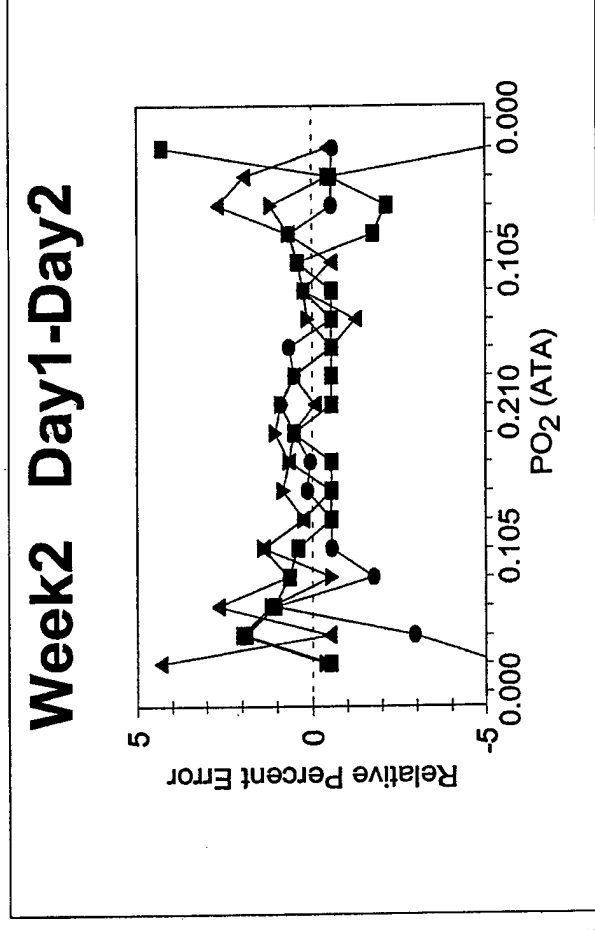
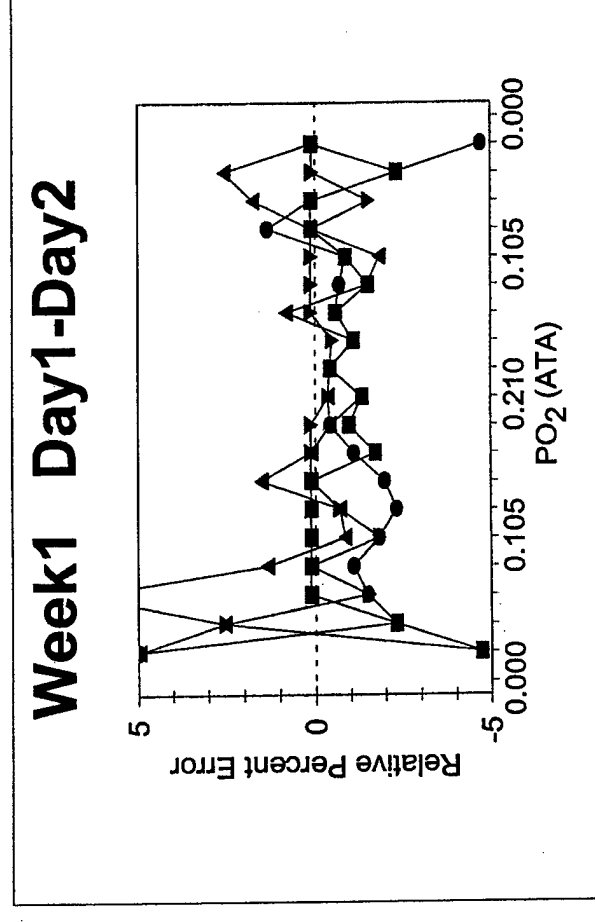
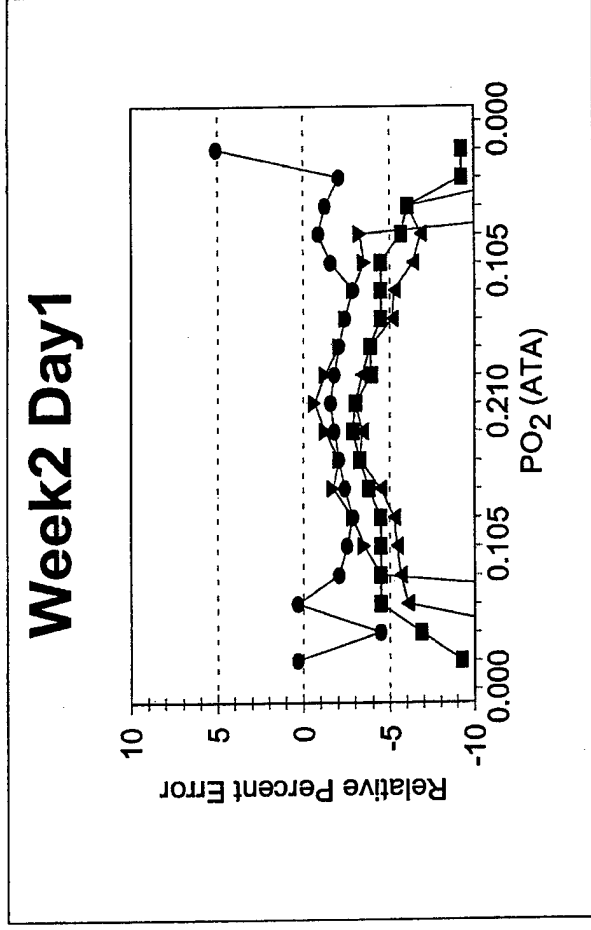
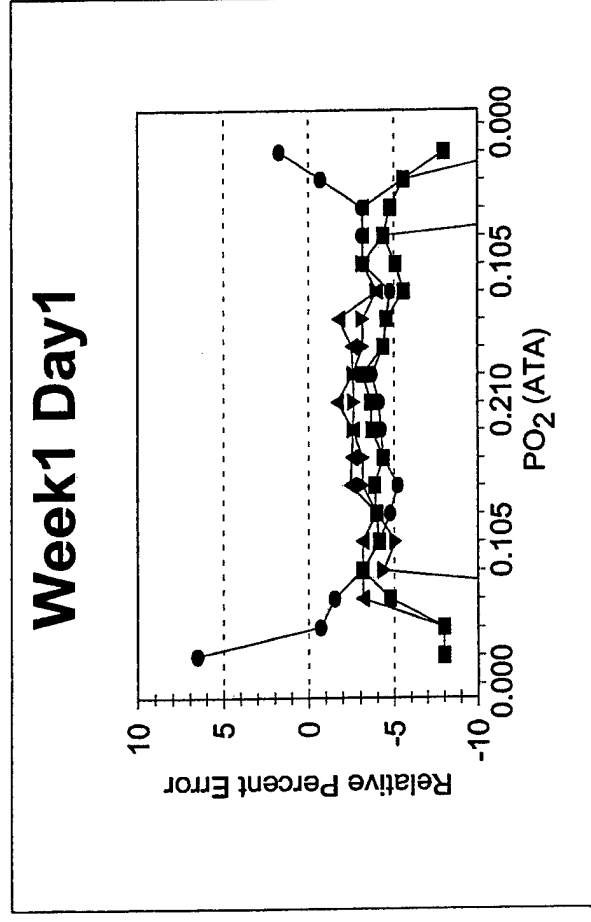


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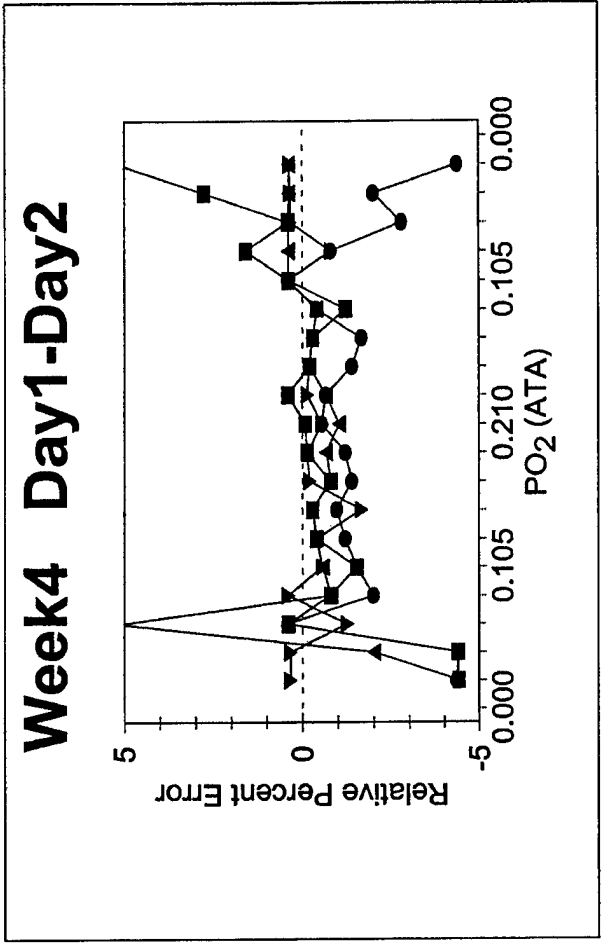
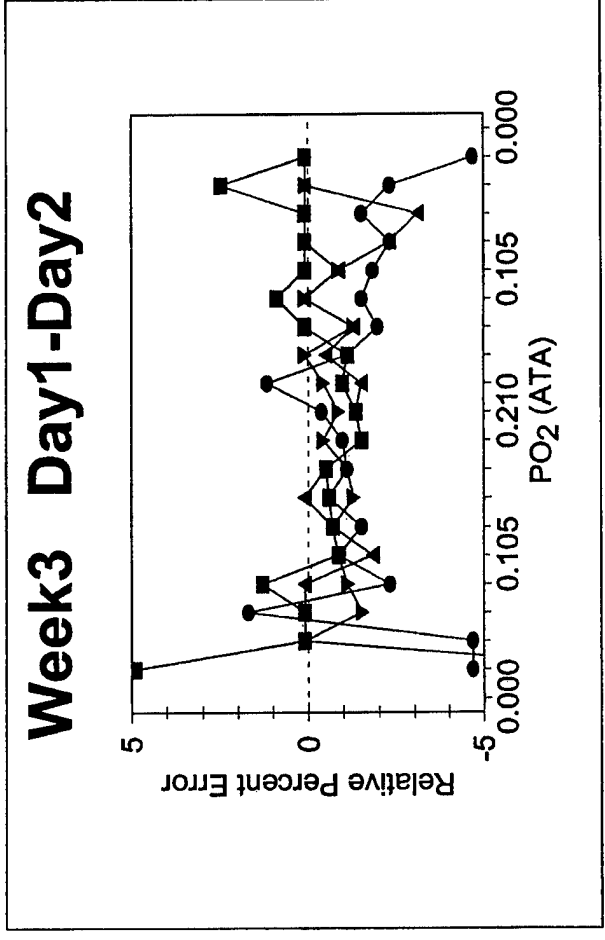
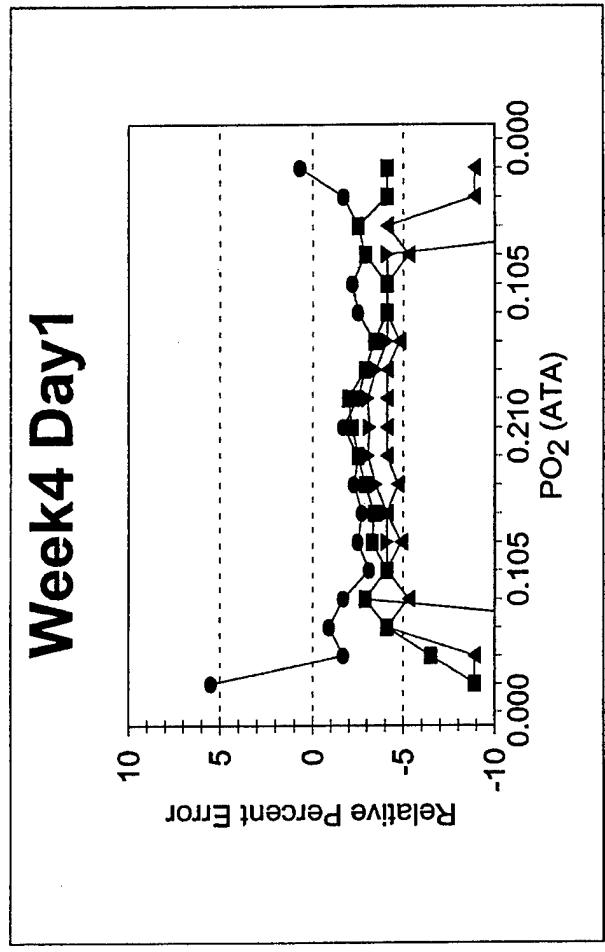
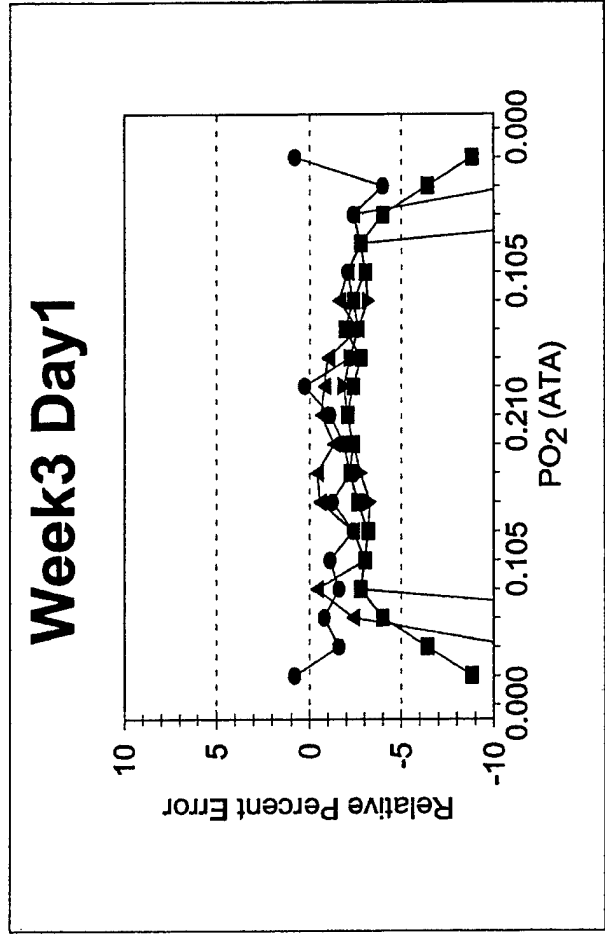


Figure 5. CO₂ ambient pressure accuracy.

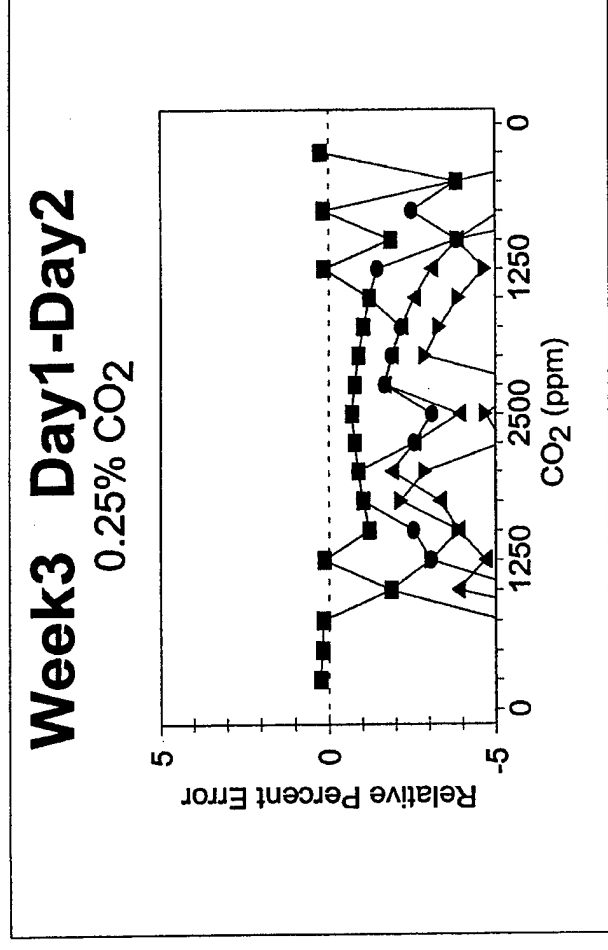
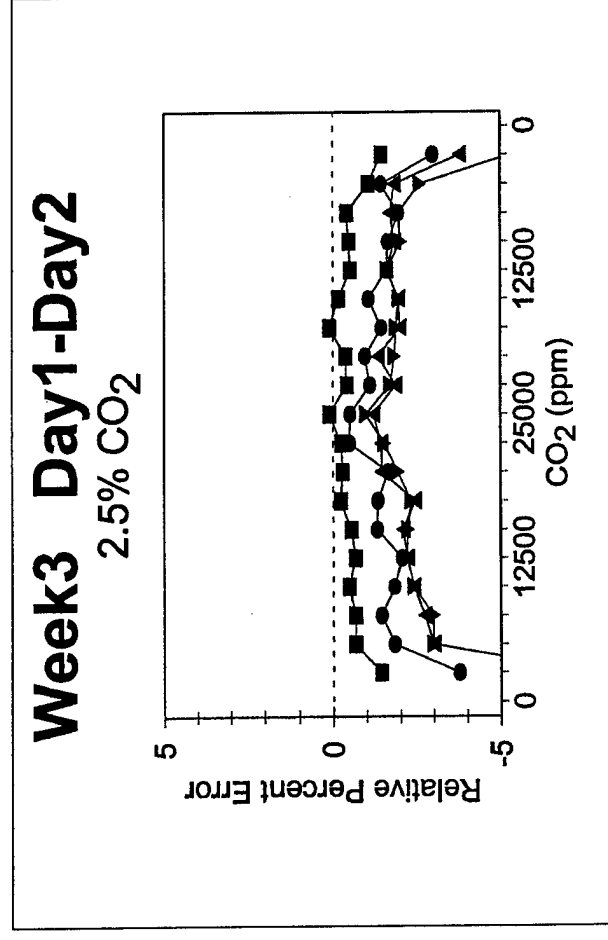
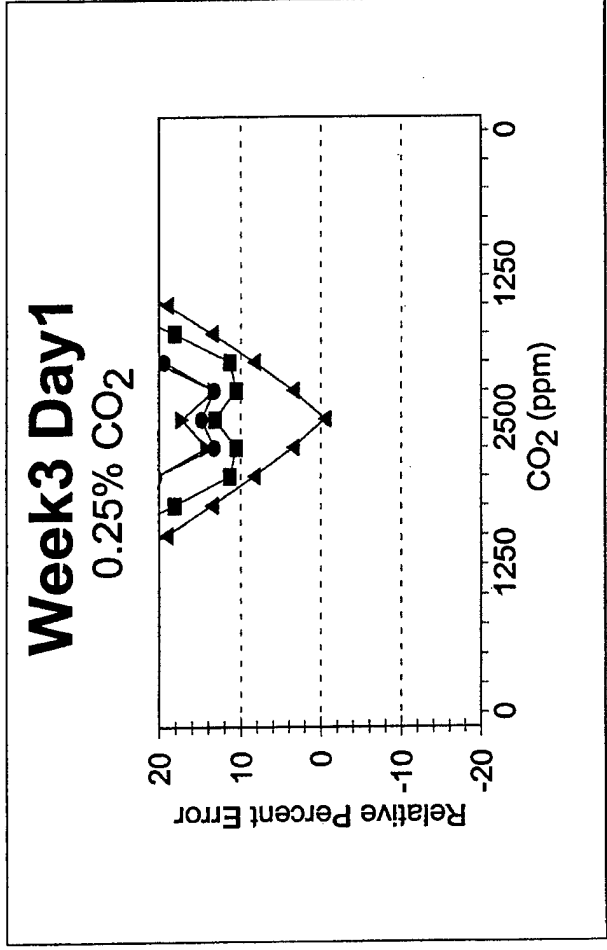
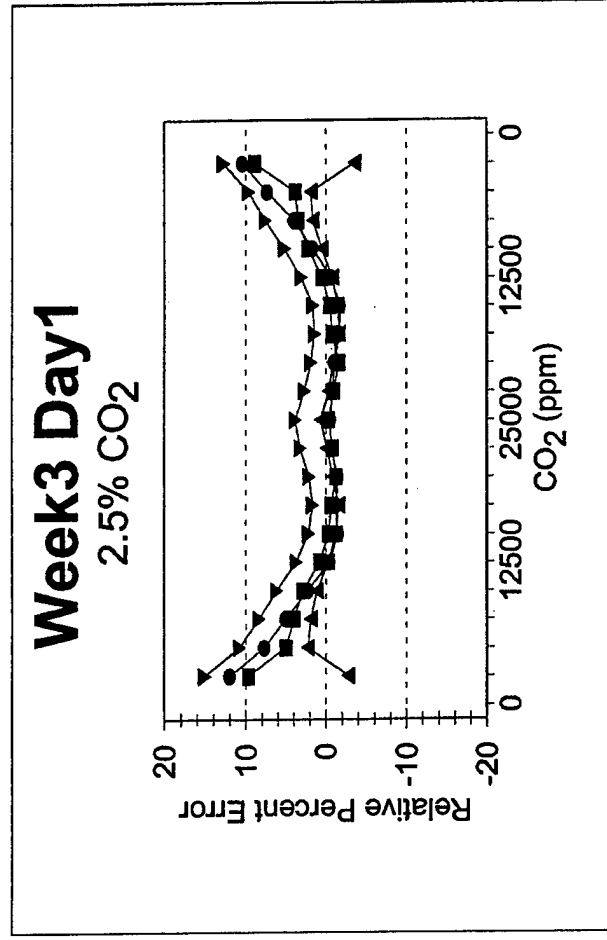


Figure 6. O₂ hyperbaric accuracy.

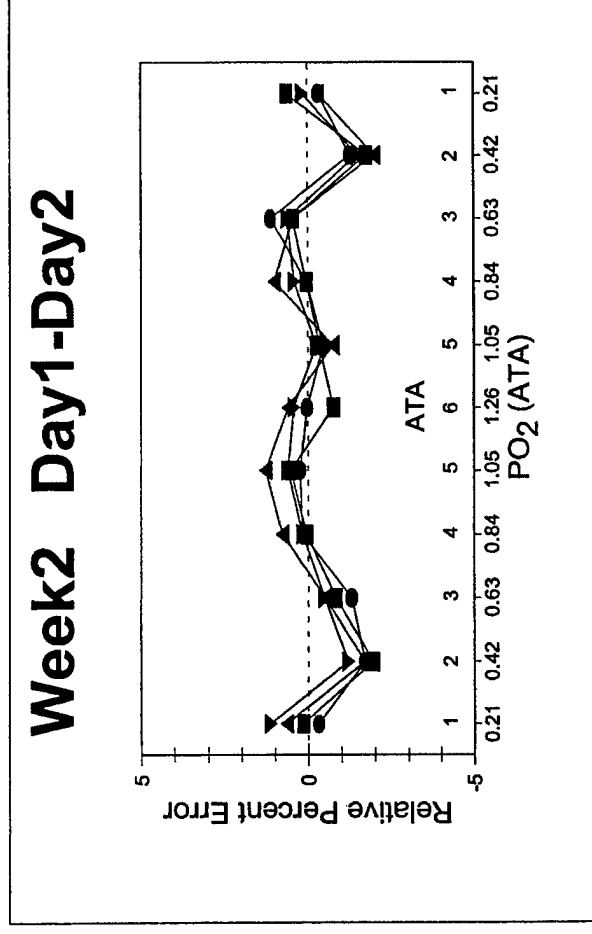
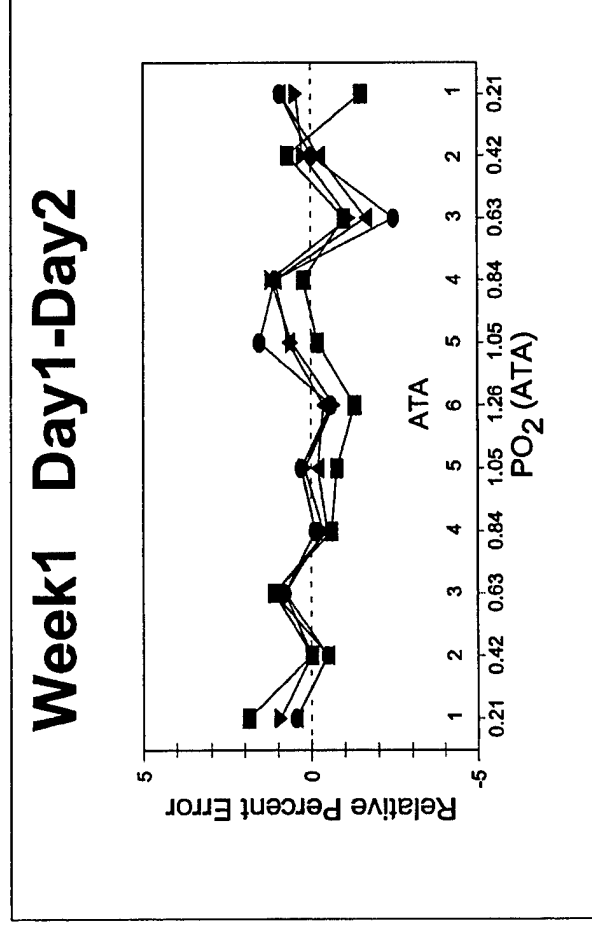
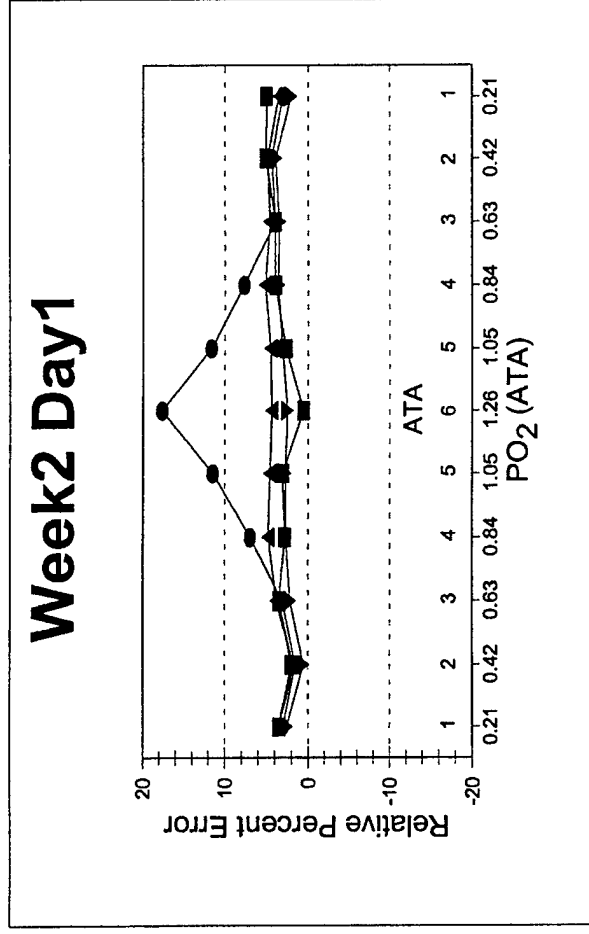
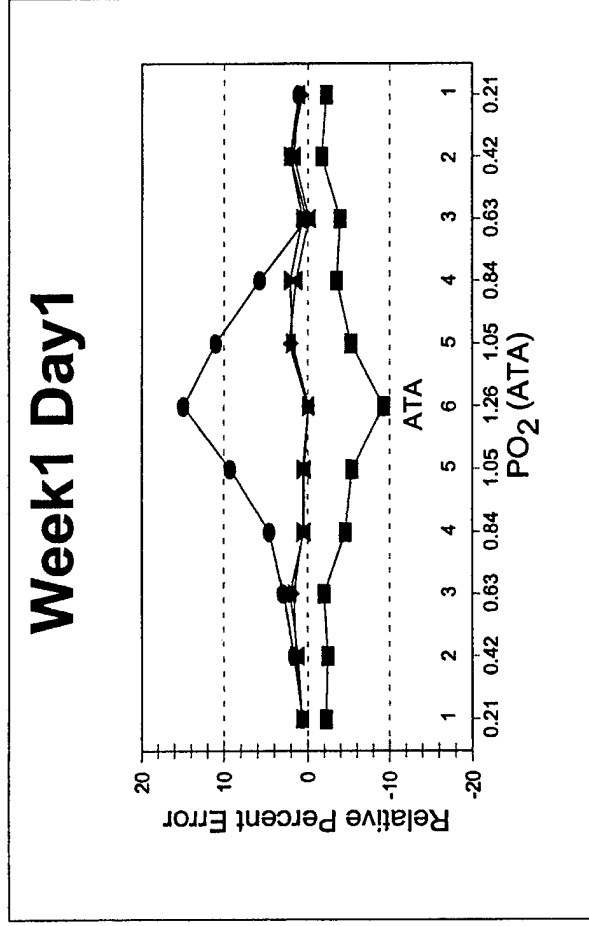


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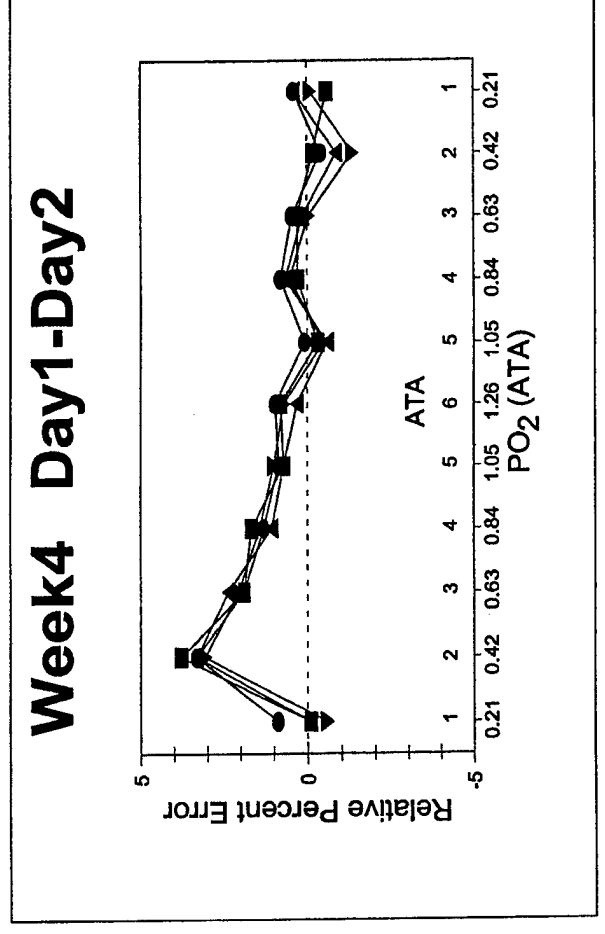
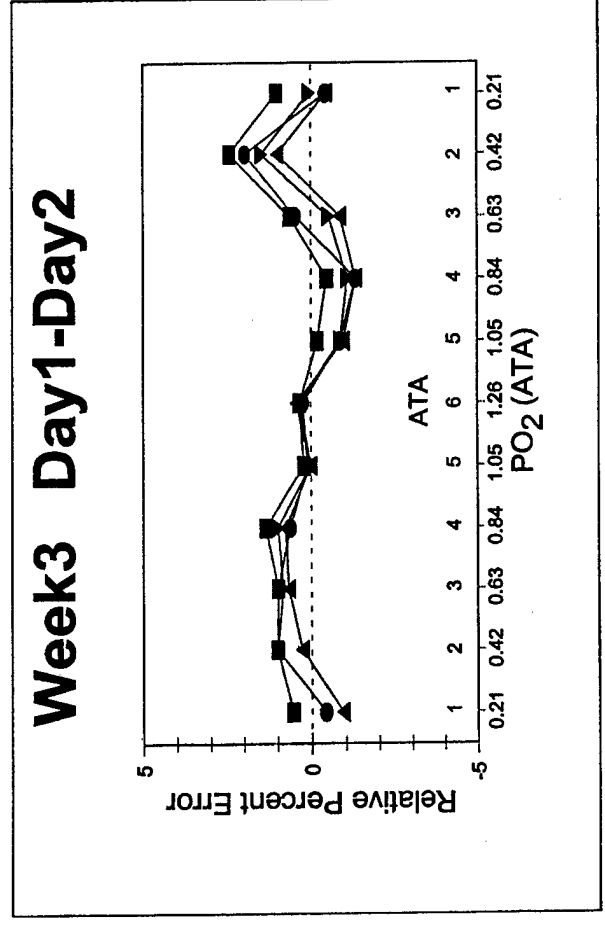
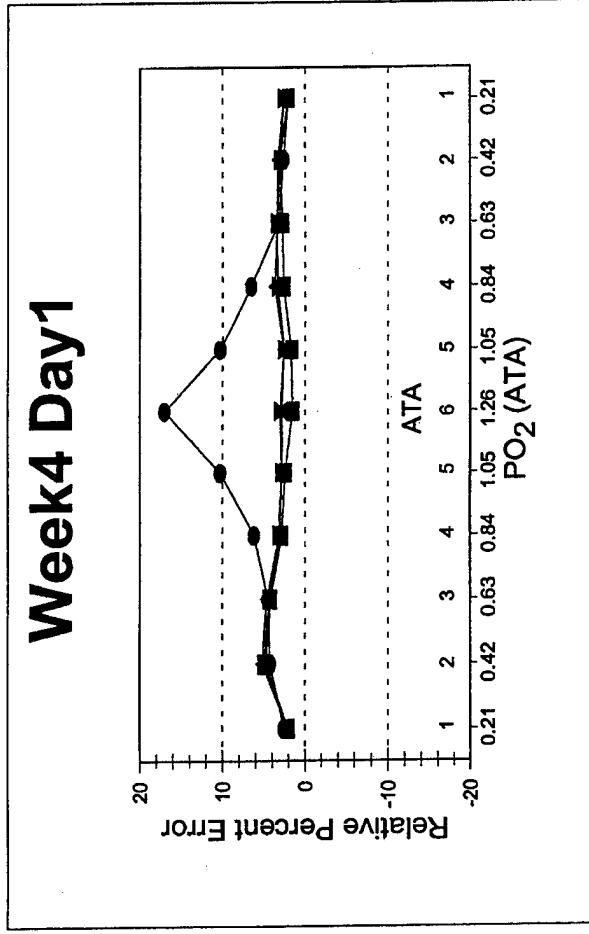
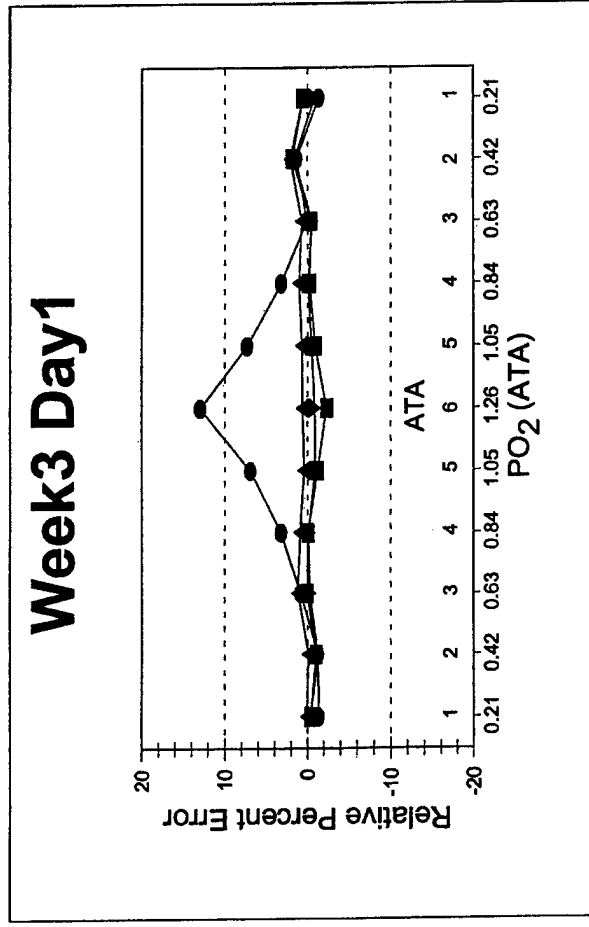


Figure 7. O₂ hyperbaric accuracy - factory calibration.

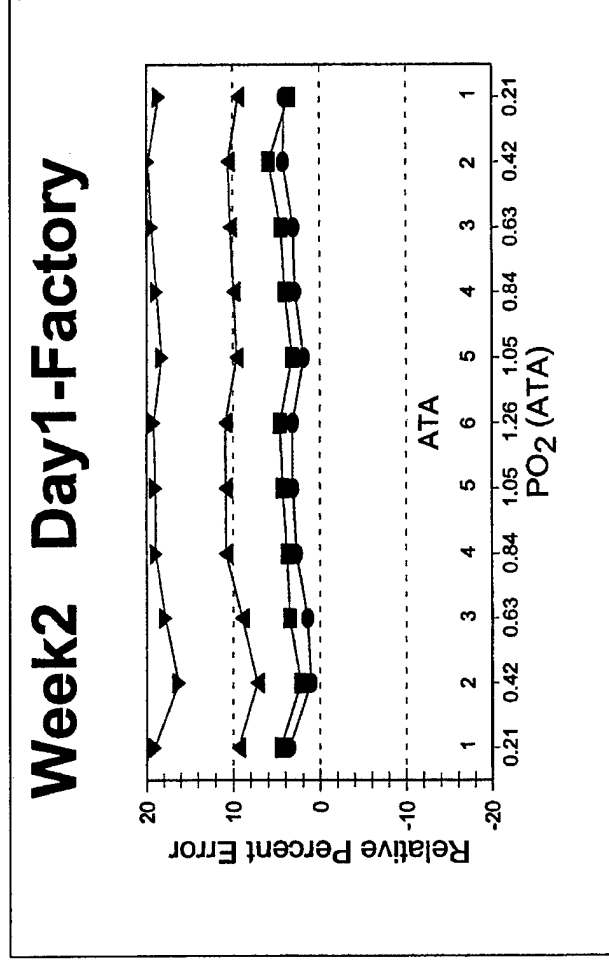
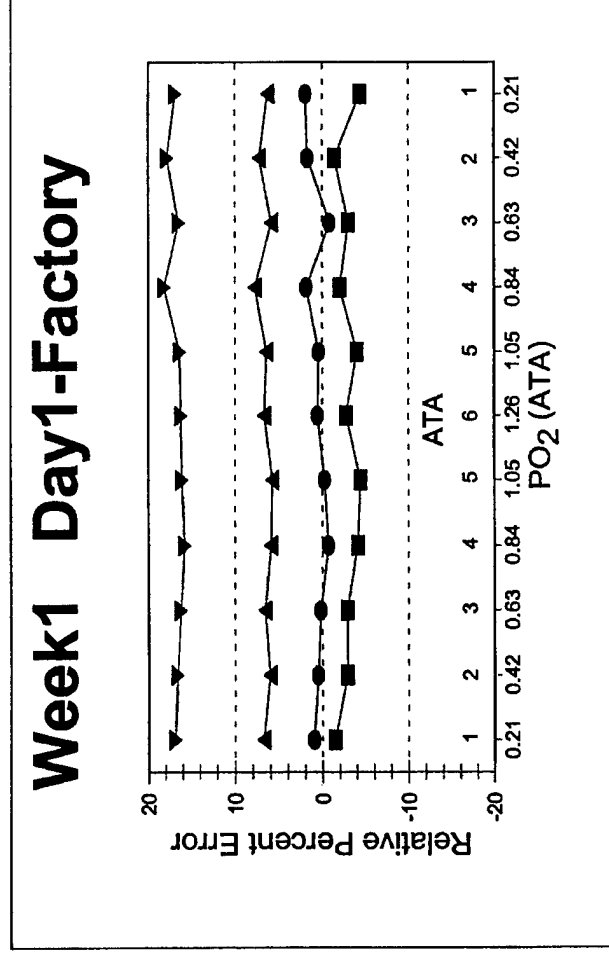
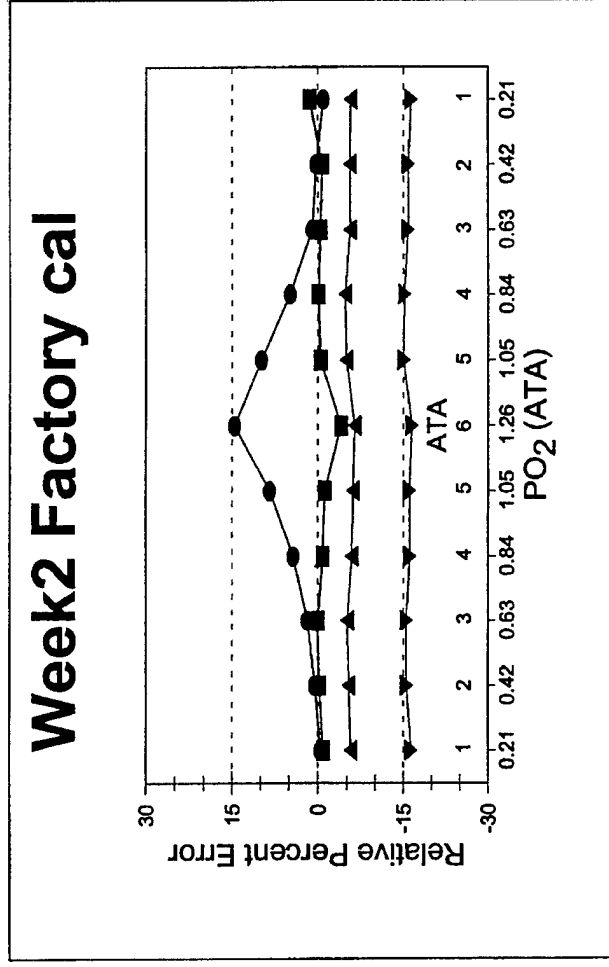
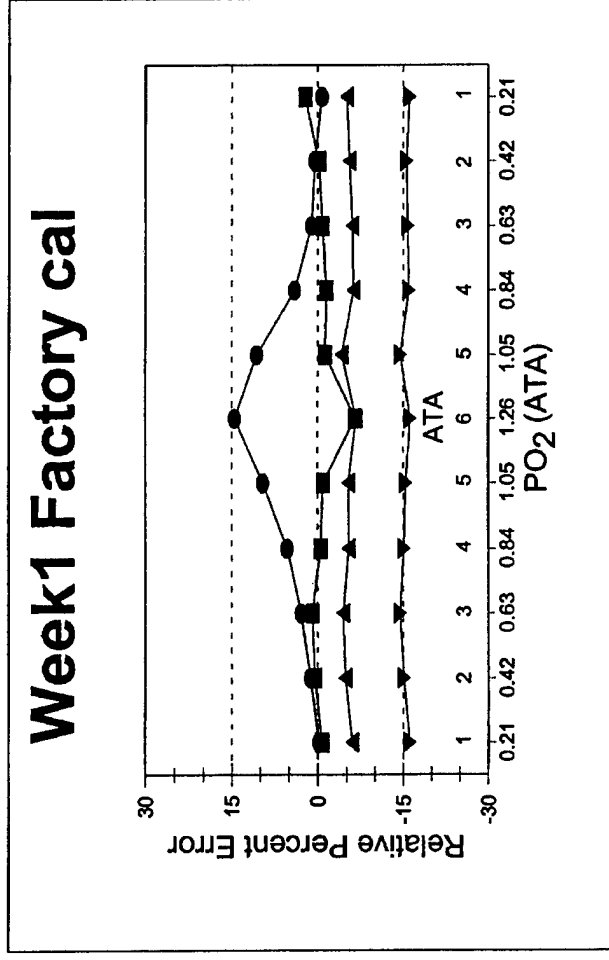


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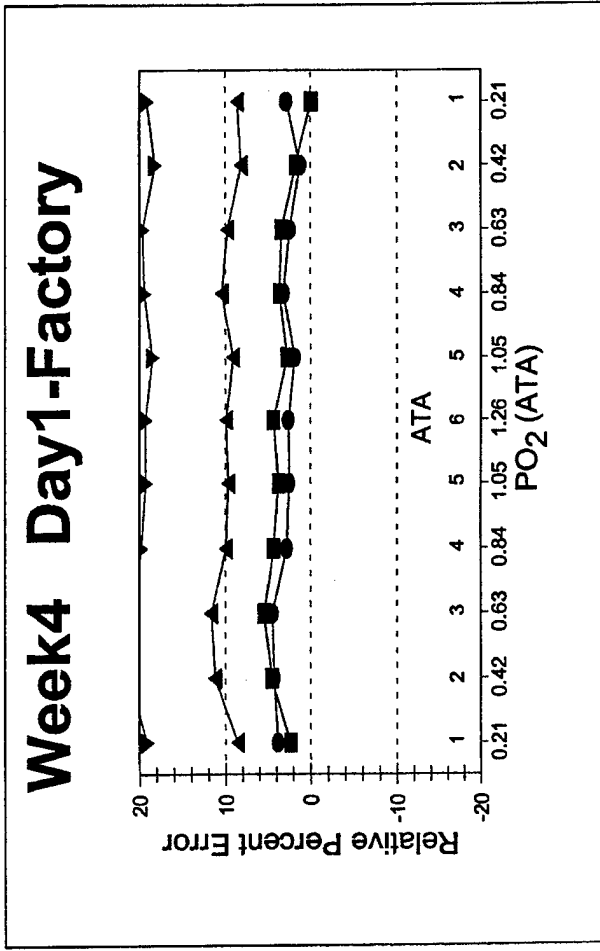
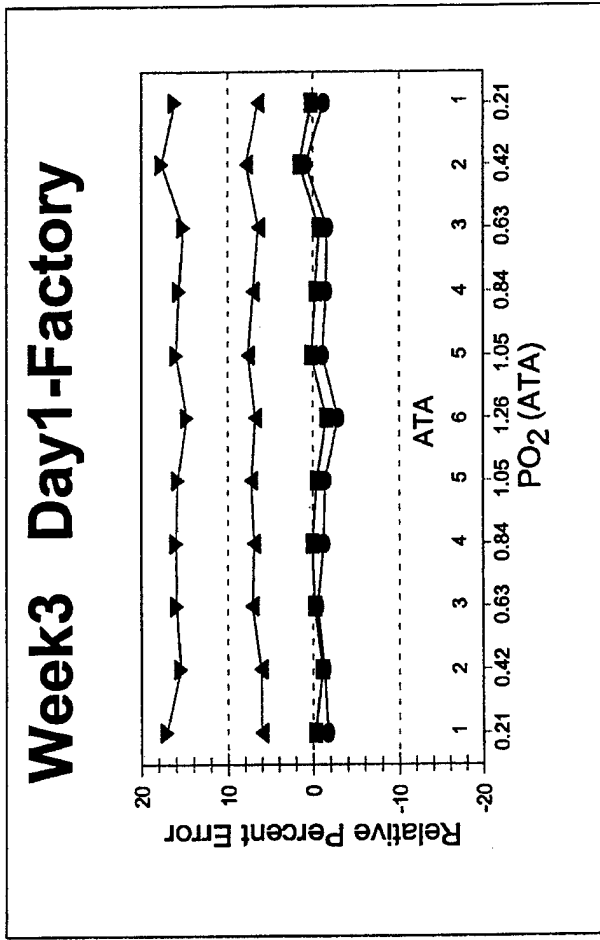
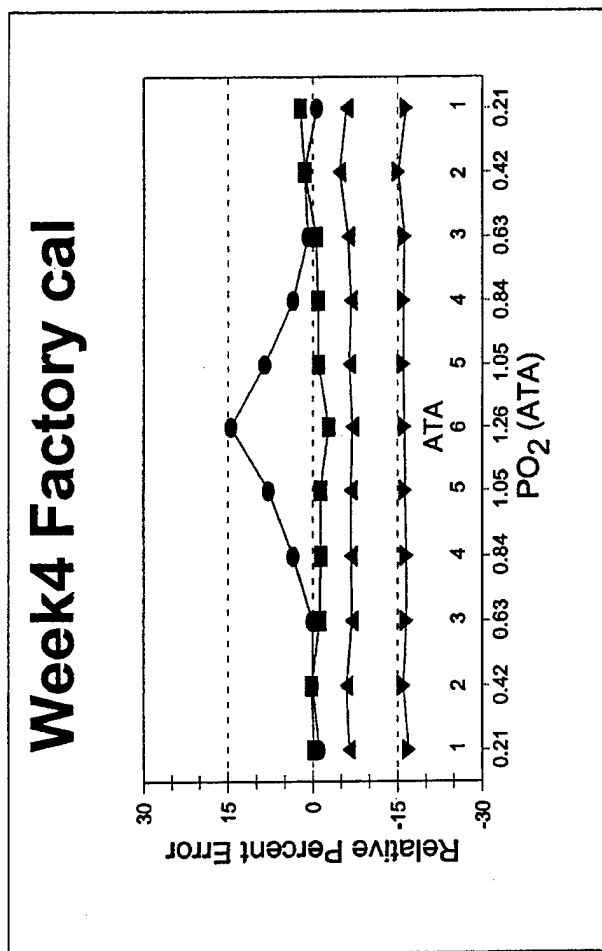
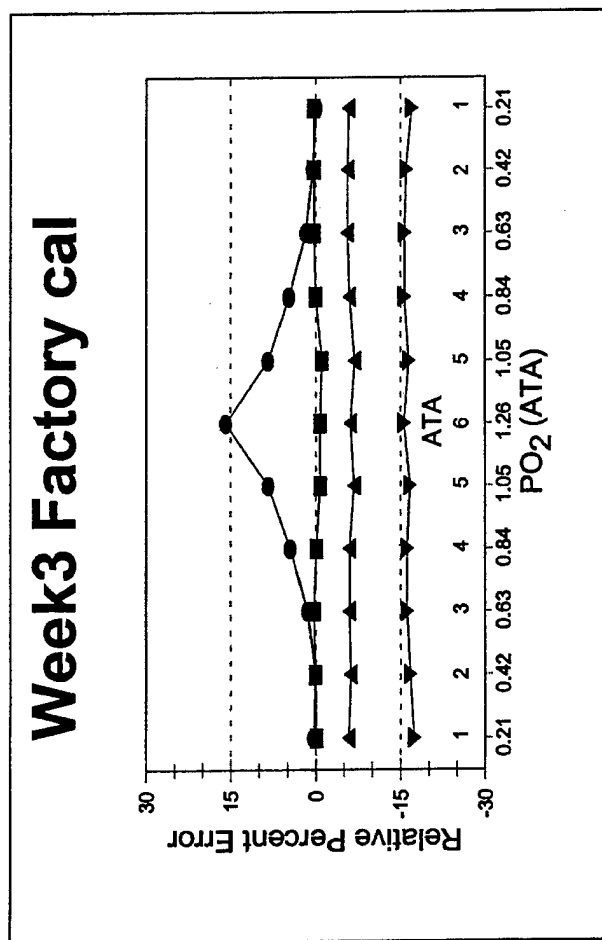


Figure 8. CO₂ hyperbaric accuracy.

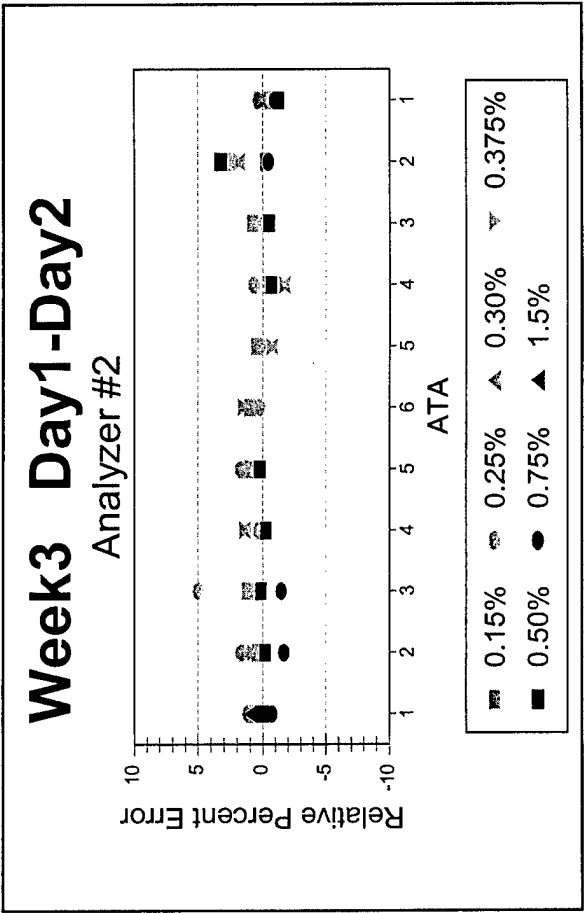
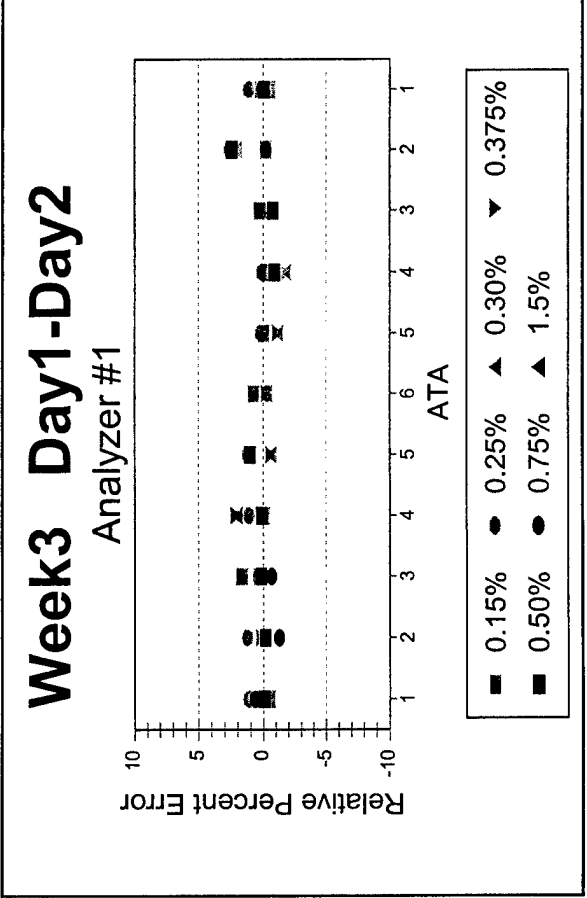
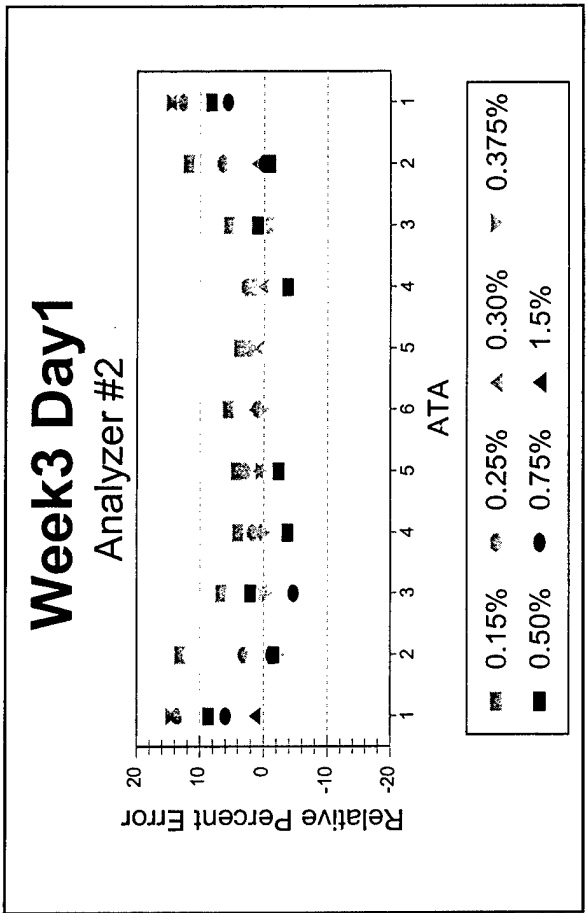
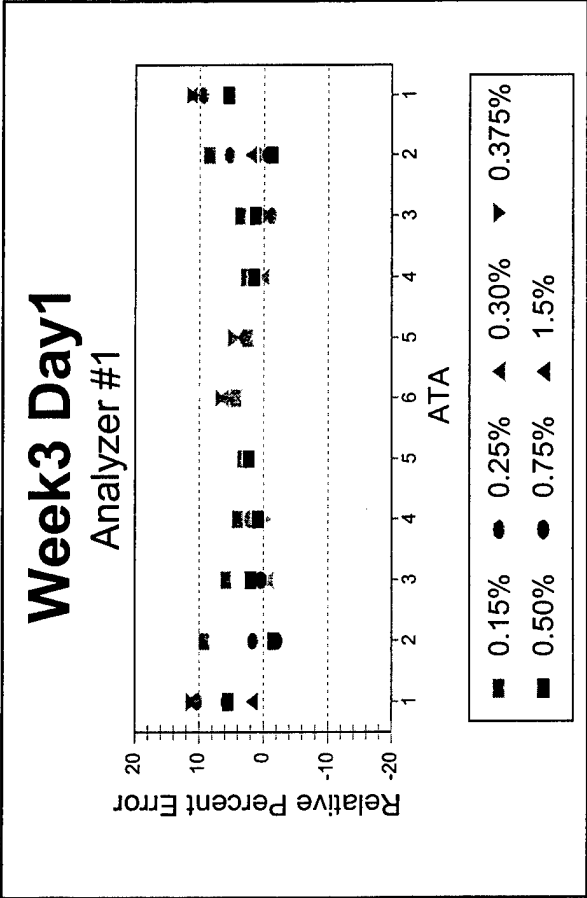


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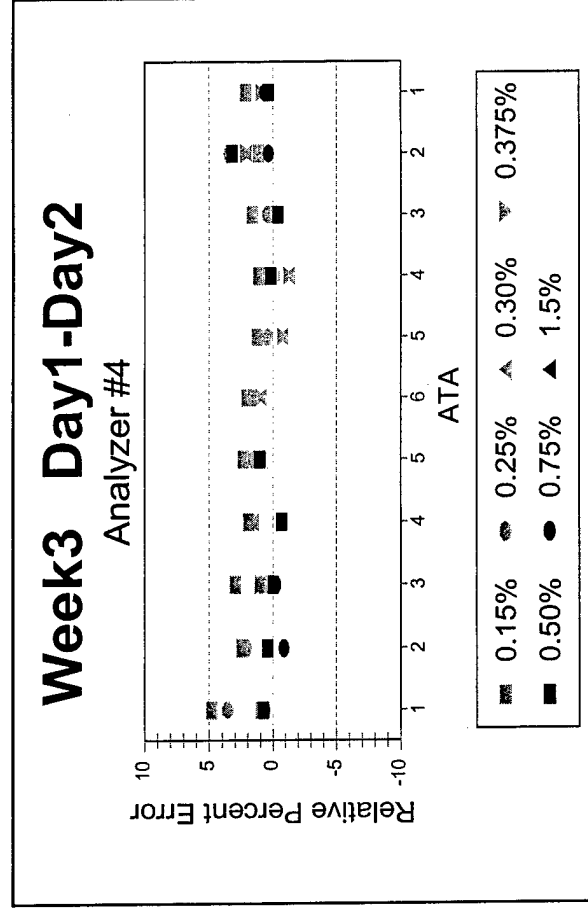
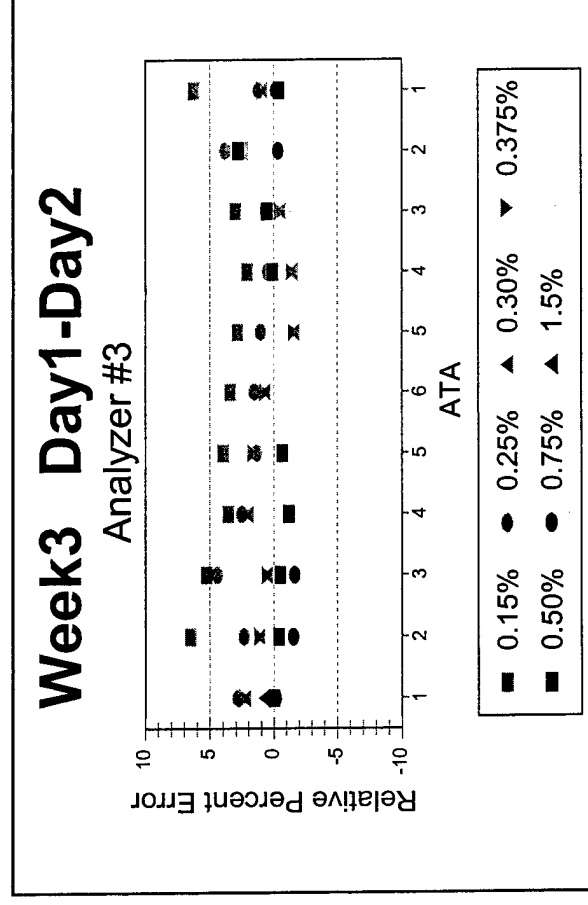
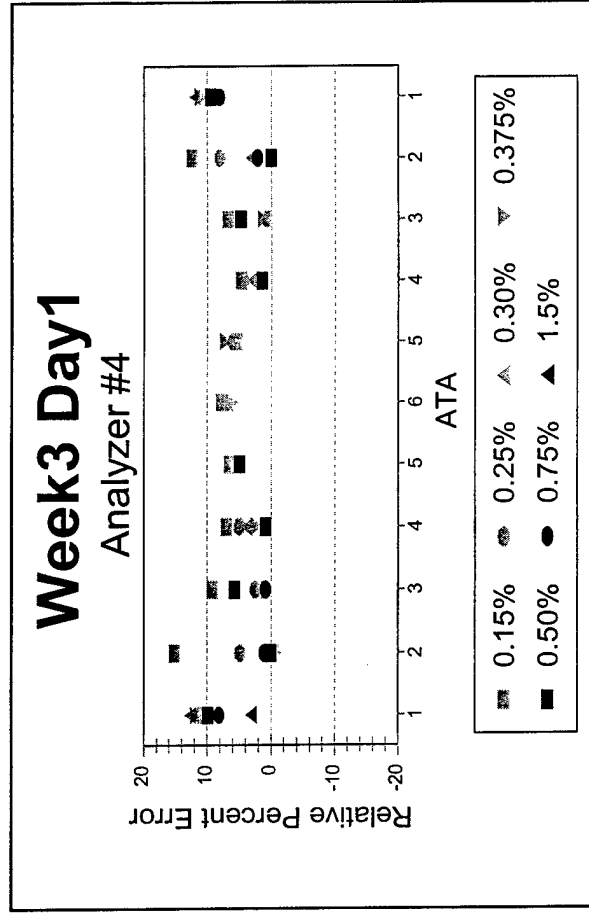
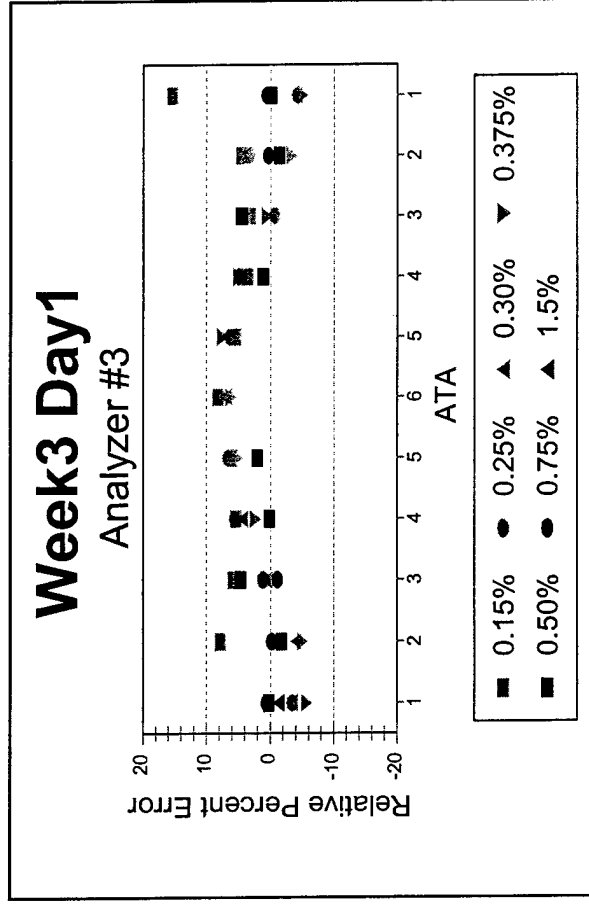


Figure 9. CO₂ hyperbaric accuracy - factory calibration.

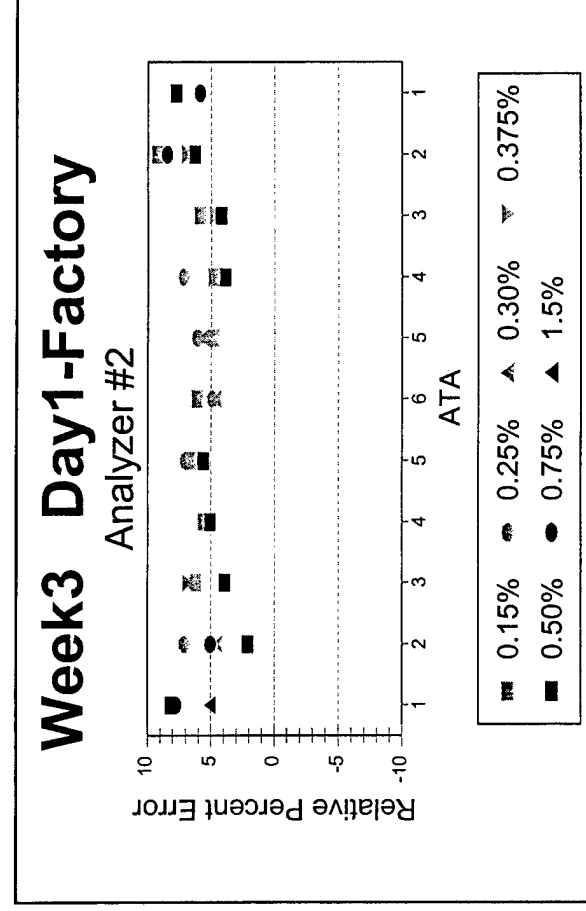
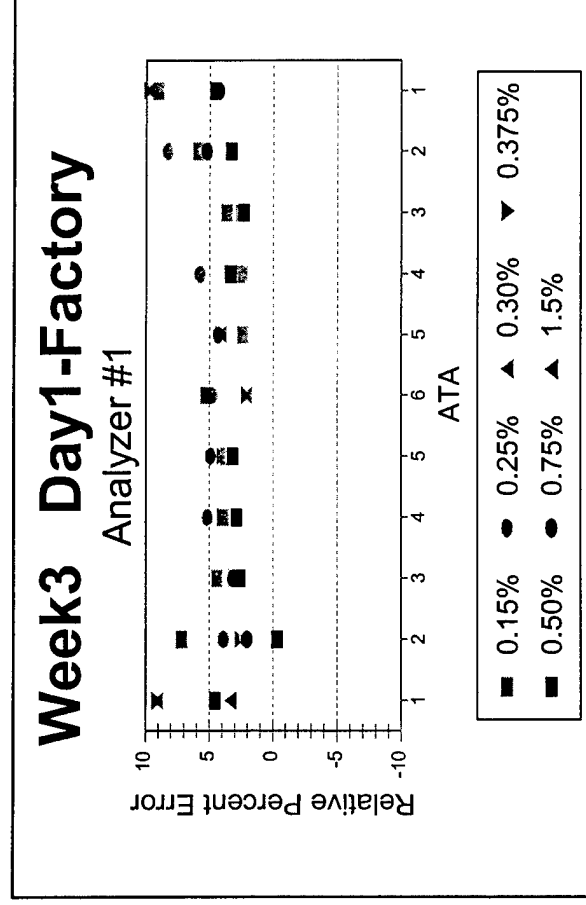
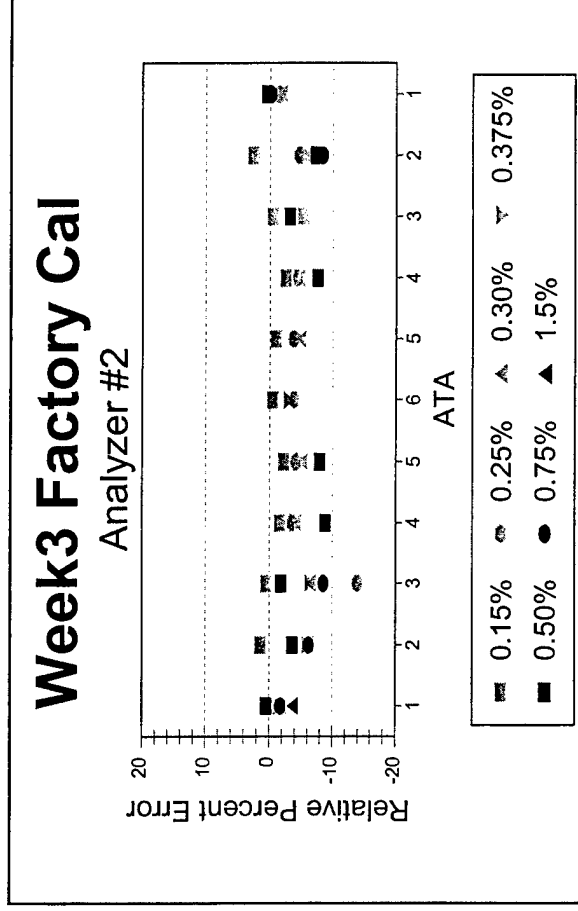
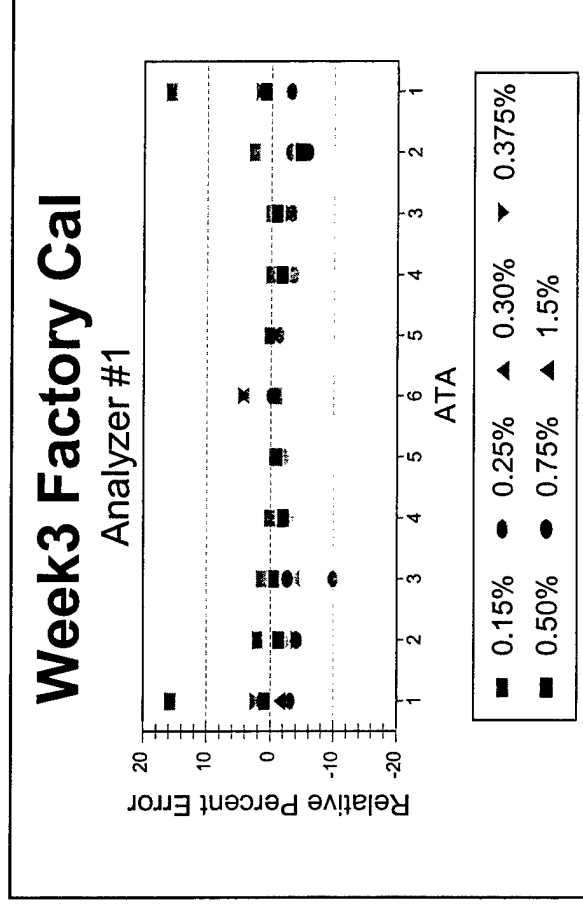


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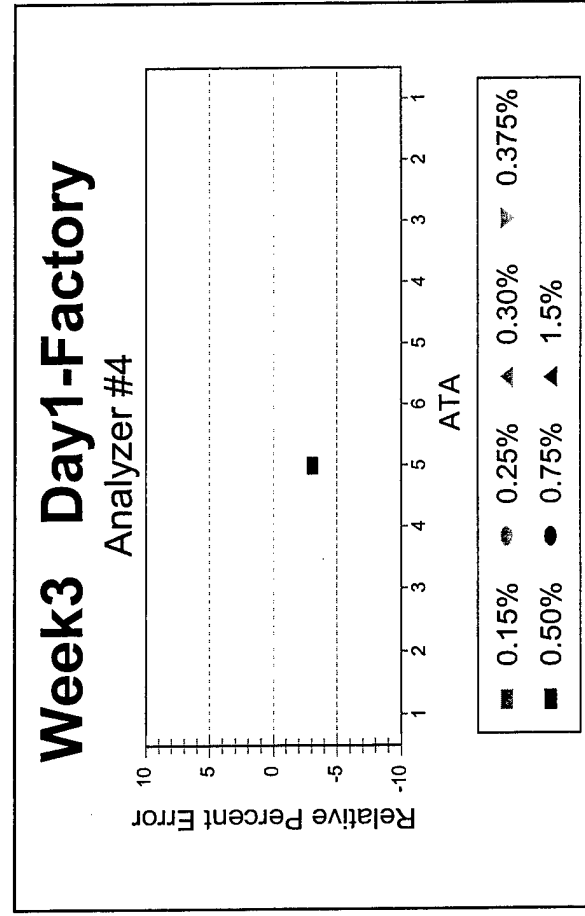
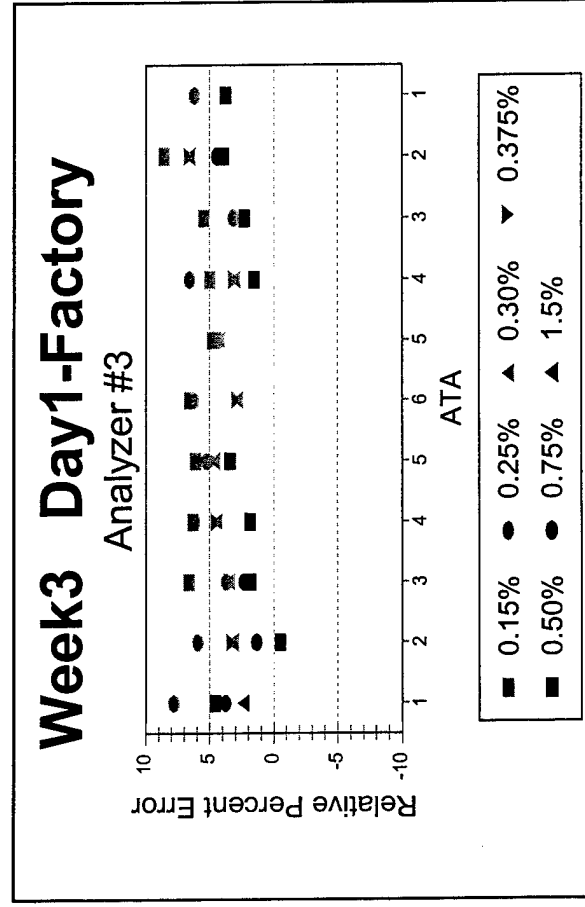
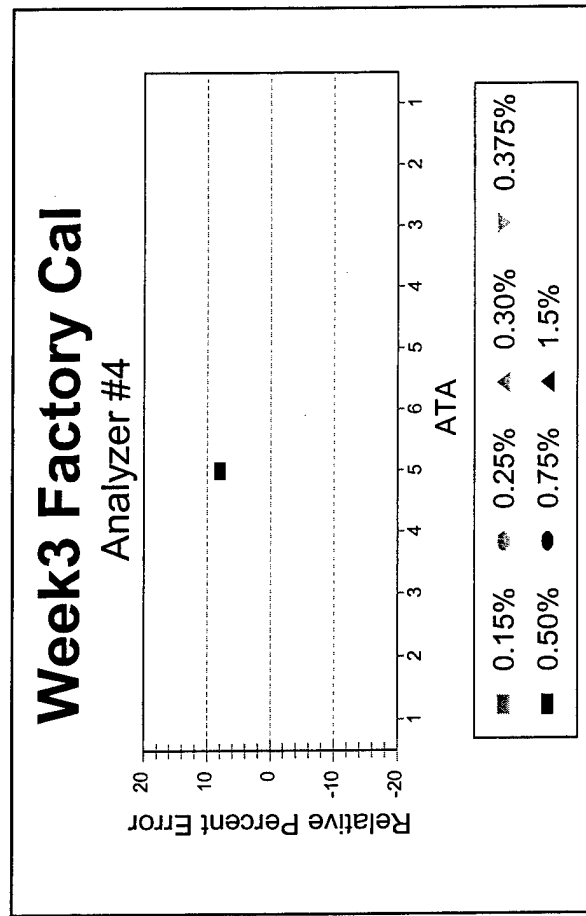
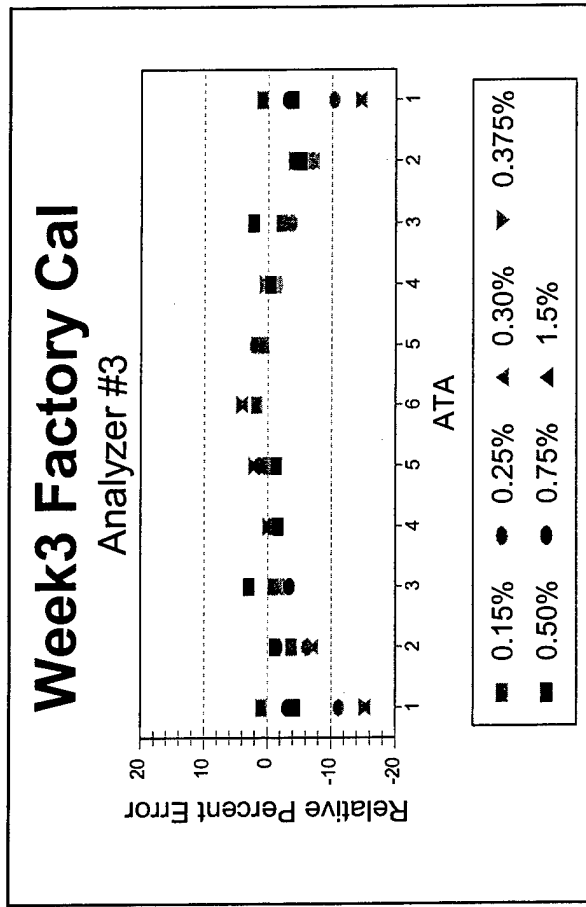


Table 1. Gas standards and test pressures used during hyperbaric testing.

CO₂ values in the table are SEV concentrations delivered to the analyzer.

Chamber pressure (ATA)	CO ₂ concentration (ppm)						PO ₂ concentration 0.209 ATA
	1,500	2,500	3,000	3,750	5,000	7,500	15,000
1	1,500	2,500	3,000	3,750	5,000	7,500	15,000
2	3,000	5,000	6,000	7,500	10,000	15,000	0.418
3	4,500	7,500	9,000	11,250	15,000	22,500	0.627
4	6,000	10,000	12,000	15,000	20,000		0.836
5	7,500	12,500	15,000	18,750	25,000		1.045
6	9,000	15,000	18,000	22,500			1.254

Bold values are current DDS CO₂ limits.

Table 2. O₂ ambient pressure precision.

	Week 1	Week 2	Week 3	Week 4
Analyzer #1				
Mean (ATA)	0.119	0.118	0.120	0.119
R.S.D. (%)	0.00	0.45	0.58	0.45
Range	0.119	0.117 - 0.120	0.118 - 0.121	0.117 - 0.120
Analyzer #2				
Mean (ATA)	0.120	0.123	0.119	0.121
R.S.D. (%)	0.97	0.00	0.45	0.73
Range	0.120 - 0.121	0.123	0.118 - 0.120	0.120 - 0.122
Analyzer #3				
Mean (ATA)	0.121	0.122	0.123	0.120
R.S.D. (%)	1.09	0.84	0.57	0.91
Range	0.120 - 0.122	0.121 - 0.122	0.122 - 0.124	0.121 - 0.122
Analyzer #4				
Mean (ATA)	0.121	0.123	0.121	0.120
R.S.D. (%)	0.96	0.69	0.46	0.46
Range	0.121 - 0.122	0.122 - 0.124	0.119 - 0.121	0.120 - 0.121

Nominal PO₂ = 0.12 ATA
R.S.D. = relative standard deviation
n=5 in all cases

Table 3. CO₂ ambient pressure precision.

	Week 1	Week 2	Week 3	Week 4
Analyzer #1				
Mean (ppm)	15280	15160	15220	15140
R.S.D. (%)	0.26	0.24	0.06	0.13
Range	15241 - 15340	15120 - 15180	15200 - 15260	15100 - 15200
Analyzer #2				
Mean (ppm)	15460	15320	15280	15460
R.S.D. (%)	0.20	0.14	0.12	0.11
Range	15420 - 15500	15280 - 15340	15240 - 15360	15400 - 15500
Analyzer #3				
Mean (ppm)	15380	15260	15300	15860
R.S.D. (%)	0.15	0.32	0.06	0.35
Range	15380 - 15400	15220 - 15260	15280 - 15300	15820 - 15880
Analyzer #4				
Mean (ppm)	15340	15240	15280	15840
R.S.D. (%)	0.26	0.27	0.14	0.11
Range	15320 - 15360	15220 - 15260	15200 - 15340	15820 - 15860

R.S.D. = relative standard deviation
n=5 in all cases

APPENDIX A

OPERATING PROCEDURES FOR THE HYPERBARIC CO₂/O₂ ANALYZER

Sufficient information is provided here to calibrate and measure CO₂ and O₂ during DDS operations onboard a submarine. It is assumed that the calibration and zero gases will be brought onboard by the SDV personnel. However, the ship's CAMS-I calibration gas (1.2-1.5% CO₂, 20-22% O₂) can be used as a backup if the normal calibration gas runs out.

Batteries/Charging.

The CO₂/O₂ analyzer is run off its self-contained NiCad batteries. When the batteries require charging, the analyzer is attached to the charger, which plugs into 110-volt line current outside of the DDS. Ideally, NiCad batteries should be fully discharged and recharged during use rather than continually topped off without a full discharge. However, this probably will not be possible and the best approach is to check the battery well before an operation (described below) to allow time for 24 h charging if the battery is low. Complete recharging should provide approximately 12 hours of usage. Note: The instrument must have batteries in place to operate.

Calibration Gas and Equipment.

Two charged high-pressure cylinders (one as a spare) of calibration gas containing ~15,000 ppm (~1.5%) CO₂ in hydrocarbon-free air (~20.9% O₂, primary gravimetric standard with accuracy guaranteed to +/-1% relative) and two charged high-pressure cylinders (one as a spare) of zero N₂ (CO₂-free, hydrocarbon-free) are needed. Cylinders should preferably contain at least 30 ft³ of gas to ensure an adequate volume for repeated calibrations. Two high-purity regulators (stainless steel diaphragm, 0-50 psi delivery pressure) with appropriate CGA fittings will be needed to install onto the cylinders. Gas mixtures and regulators can be obtained from: 1) Scott Specialty Gases, Plumsteadville, PA; 2) Air Products and Chemicals, Inc., Allentown, PA; or 3) MG Industries, Specialty Gas Division, Malvern, PA; as well as from other suppliers.

Tygon or rubber tubing (~3/16 inch inner diameter) and plastic Ys are used to construct the calibration tubing.

Battery/Calibration Check and Re-calibration (If necessary).

1. A battery/calibration check needs to be done, as described below, prior to each day's (operation) use.
2. Locate the calibration and zero gases and install the regulators if not already in place. Purge the regulators three times to ensure removal of all ambient air, then dial in a delivery pressure of several psig. Leave gas cylinders turned on but secure flow using the regulator outflow valve.

3. Disconnect analyzer from charger.
4. Turn on analyzer by pressing the red key. The LCD will show the company name, model number, and information on key functions.
5. Press the "0" key to exit that screen. The LCD display will show the following choices:
 - 1- General Utilities
 - 2- Read/Store Data
 - 3- View/Print Data
 - 4- Download Data
6. Press "1" (General Utilities). The display will show the following:
 - 1- Time/Date
 - 2- Battery Status
 - 3- Memory
 - 9- More 0- Exit
7. Battery check. Batteries should be checked without the charger connected. Press "2" to read the available battery capacity. If there is insufficient charge (<50%), the analyzer should be charged.
8. Attach a short (<1 foot) length of Tygon or rubber tubing that contains a Y with a side branch of approximately six inches to the calibration gas. Connect the inlet port of the CO₂/O₂ analyzer to the side branch of tubing so that calibration gas can be sampled without pressurizing the analyzer. (See figure at the end of this appendix.)
9. Press "0" twice and then "2" twice to read gas level. Press "5" to turn on pump. Analyzer is now measuring CO₂ and O₂. Allow to warm up for five minutes.
10. Open the calibration regulator valve and adjust gas flow so it is just audible as it exits the overflow.
11. Wait at least one minute for reading to stabilize. Analyzer display is in ppm CO₂ SEV and ppATA O₂.
12. If readings are within 400 ppm CO₂ and 0.005 ppATA O₂ of the calibration gas, calibration is unnecessary; go to step #18.
13. If calibration is necessary, press "0" to exit screen, "1" (General Utilities), "9" (More), "4" (Calibration), "1" (CO₂), "5" (Pump), "1" (Calibrate).
14. Enter CO₂ concentration (e.g., 15,000 ppm = 1.5%). To backspace over an entry mistake, press and hold "0".

15. Press "0" to exit screen and then "1" (Yes) to calibrate. CO₂ is now calibrated. Observe readout. Analyzer should be within 400 ppm of the calibration value. Calibration can be repeated if needed.
16. To calibrate O₂, attach analyzer to zero N₂ and adjust flow as before. Press "0" to exit screen, "2" (PO₂), "1" (Zero PO₂), "5" (Pump). Allow reading to stabilize. Press "1" (Zero Level). Analyzer should display "Zeroed O₂". Observe readout, analyzer should read 00.000 ppATA O₂; if not, repeat zero procedure.
17. Reattach calibration gas and adjust flow. Press "0" (Exit), "2" (PO₂), "2" (Calibrate O₂ Span), "5" (Pump). Allow readings to stabilize. Press "1" (Enter Gas Con), enter O₂ concentration (e.g., 00.209 ppATA = 20.9%), "0" (Enter), "1" (Yes). Observe readout. Analyzer should be within 0.005 ppATA of the calibration value. Calibration can be repeated if needed.
18. Shut off gas flow, close valve on the cylinder, and bleed regulator down. Turn off analyzer by pressing red key to conserve batteries. Remove tubing from analyzer.
19. The analyzer is ready to be taken into the DDS.

Use during DDS Operations.

1. To begin measuring CO₂/O₂, simply turn on the instrument by pressing the red key, press "0", then "2" twice (Read Gas Levels), then "5" (Pump On); allow to warm up five minutes before using.
2. Pressure (fsw) can be displayed in place of O₂ by pressing "1" and cycling through the options. The accuracy of the pressure reading shown on the analyzer's display is unknown.
3. During the DDS operation, the analyzer can be turned off during periods of non-use, and turned back on and allowed to warm up five minutes before measuring CO₂/O₂.

If Dropped in the Water.

1. If the analyzer is dropped into the water, it will float. If the pump is operating, water may be drawn into the inlet filter located on one side of the case and flow will stop. A flow sensor inside the analyzer will then detect the absence of gas flow and turn the pump off within several seconds.
2. To put the analyzer back into operation, the filter is first removed by unscrewing the retaining nut and gently pulling it out using your fingers. The filter then can be replaced or simply blown out by mouth or with a gentle flow of gas.
3. Normal startup procedure is then followed.

Cold Start (When there is a suspected problem).

1. When there is a suspected problem with the analyzer, the cold start option reboots the software and often restores the analyzer to normal operation. Problems often cured with a cold start include: 1) analyzer not responsive to key strokes, and 2) analyzer display indicates that it will not accept the calibration value that is entered.
2. Cold start procedure:
 - a. Hold the "3" key and turn the analyzer on by pressing the red key.
 - b. The display should show "Cold Start". Press "1" to continue.
 - c. After a cold start, the alarm values must be re-entered or the analyzer will beep and show "Max" on the display.
 - d. Press "0" to exit from the information display, "1" (General Utilities), "9" (More), and "5" (Alarm Levels).
 - e. Press "2" (Max) and "1" (Change CO₂).
 - f. Enter a value of 26,000 ppm (or other selected concentration), then press "0" (Set).
 - g. Press "2" (Max), "2" (Change O₂).
 - h. Enter a value of 00.210 (or other selected concentration), then press "0" (Set).
 - i. Press "0" twice to return to main menu.

Factory Calibration (When calibration gas is unavailable or suspect).

1. When no calibration gas is available or a problem with the gas on hand is suspected, the analyzer can be reset to the default factory calibration.
2. Reset to factory calibration procedure:
 - a. Turn the analyzer on by pressing the red key.
 - b. Press "0" to exit from the information display, "1" (General Utilities), "9" (More), "4" (Calibration), and "5" (Factory Settings).
 - c. Press "1" (Yes) when prompted: "CAUTION, Returning to factory setting of calibration and zero?"
 - d. Press "0" twice to return to the main menu.

Factory Repair/Maintenance Service.

1. Analyzers are kept under service contract with the manufacturer (Geotechnical Instruments). This contract needs to be renewed annually (at the start of every fiscal year).

This service contract provides for the following:

- a. One planned yearly service by the manufacturer that includes re-calibration, O₂ sensor replacement, battery replacement if needed, any necessary repairs, and general checkout of instrument function.
 - b. Free software upgrades.
 - c. Hardware modifications due to product improvement, provided the modification is compatible with the current unit, at no extra charge.
 - d. Repair of any malfunction that occurs in the field, at no extra charge. This excludes excessive physical damage.
 - e. UPS shipping charges to and from Geotechnical Instruments, U.K., and the SDV sites for repairs (if needed) and yearly service. Geotechnical Instruments will provide shipping labels.
2. In the event of a problem with an analyzer that cannot be corrected by the above-suggested steps, contact the manufacturer via telephone. In the U.S., dial commercial 011-44-1926 338111. Outside of the U.S. dial commercial +44 (0)1926 338111.

Calibration setup: hyperbaric CO₂/O₂ analyzer.

